

# The American Mineralogist

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Nos. 7 and 8

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# THE AMERICAN MINERALOGIST

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## COMPLETE SUBSTITUTION OF ALUMINUM FOR SILICON: THE SYSTEM

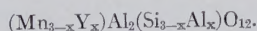


H. S. YODER AND M. L. KEITH,

*Geophysical Laboratory, Washington, D. C.*

### ABSTRACT

Thermal, optical, and  $x$ -ray data indicate that there is a complete solid solution series between spessartite,  $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$ , and yttrgarnet,  $\text{Y}_3\text{Al}_2(\text{AlO}_4)_3$ . The substitution  $\text{Y}^{+3}\text{Al}^{+3} \rightarrow \text{Mn}^{+2}\text{Si}^{+4}$  may be represented by the formula:



Yttrgarnet has a cube edge of  $12.01 \pm 0.02 \text{ \AA}$  and the space group  $O_h^{10}$ . Using the coordinates of grossularite as determined by Menzer, good agreement was obtained between calculated and observed intensities. The atomic positions are:

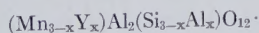
Al in 16( <i>a</i> )	0	0	0
Y in 24( <i>c</i> )	$\frac{1}{4}$	$\frac{1}{8}$	0
Al in 24( <i>d</i> )	$\frac{1}{4}$	$\frac{3}{8}$	0
O in 96( <i>h</i> )	$x$	$y$	$z$

where  $x$ ,  $y$ , and  $z$  are 0.04, 0.055, and 0.64, respectively. The yttrium is in eightfold coordination; the aluminum is in both four- and sixfold coordination. Yttrgarnet inverts to a high form, yttrioalumite, at  $1970 \pm 50^\circ \text{C}$ .

This is the first case on record of the complete substitution of aluminum for silicon in an orthosilicate. The complete solid solution series contradicts the prevalent idea that the substitution of aluminum for silicon always decreases as the Si/O ratio decreases.

### INTRODUCTION

It was pointed out by Jaffe (1950) that some natural spessartite garnets contain as much as 2.6 per cent  $\text{Y}_2\text{O}_3$ . He suggested that yttrium occupies manganese positions in the garnet structure, and that the substitution should occur as  $\text{Y}^{+3}\text{Al}^{+3} \rightarrow \text{Mn}^{+2}\text{Si}^{+4}$ . Jaffe expressed the opinion that proof of the proposed substitution might be obtained by synthesizing yttrian spessartites. The above substitution may be represented by the following formula:



When  $x=3$ , the end member becomes  $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$ . Therefore, the system  $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$  was explored experimentally.



## PREPARATION OF MIXTURES

Mixtures were made from  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{MnCO}_3$ . The silica and alumina were obtained from the prepared stock of J. F. Schairer of this Laboratory; the yttria was secured by H. W. Jaffe from A. D. Mackay and was analyzed spectrographically by M. J. Peterson of the U. S. Bureau of Mines;<sup>1</sup> the  $\text{MnCO}_3$  was C. P. Grade material from J. T. Baker Chemical Company. The powders were weighed to 0.1 mg. into a platinum crucible in the requisite proportions to make from 2 to 5 grams of the desired product. After stirring to incorporate the silica, the powder was transferred to an agate mortar and ground for a minimum of 15 minutes to insure thorough mixing. Several different methods were required to prepare further the mixtures for use in the thermal investigation. For six lower-melting mixtures, those which melted completely below  $1550^\circ$ , a portion of the powder was heated in a platinum crucible suspended in a nitrogen atmosphere, in a vertical platinum-wound resistance furnace similar to that described by Bowen and Schairer (1932, p. 183). The charge was lowered to the furnace hot spot in stages to prevent loss of material due to possible violent escape of  $\text{CO}_2$ . The preparations were held for about 15 hours at the required temperature in the nitrogen atmosphere and then quenched by dropping into mercury. For two higher-melting mixtures, the powders were pressed under several tons per square inch into the form of thin disks. Each disk was placed in a platinum crucible, heated at  $1700^\circ$  to  $1730^\circ$  for several hours in a Meker gas furnace, and the charge was then quickly cooled by placing the crucible in water. The glasses and sintered products prepared in this way were then used in the thermal investigation.

<sup>1</sup> The analysis gave:

Per cent	
>10	$\text{Y}_2\text{O}_3$
0.3 to 3	$\text{K}_2\text{O}$
0.2 to 2	$\text{SmO}_2$
0.02 to 0.2	$\text{Dy}_2\text{O}_3$ , $\text{Ce}_2\text{O}_3$ , $\text{Gd}_2\text{O}_3$ , $\text{PrO}_2$
0.01 to 0.1	$\text{ZrO}_2$ , $\text{La}_2\text{O}_3$ , $\text{Nd}_2\text{O}_3$ , $\text{HfO}_2$ , $\text{Na}_2\text{O}$
0.005 to 0.05	$\text{Sc}_2\text{O}_3$
<0.01	$\text{Al}_2\text{O}_3$ , $\text{Fe}_2\text{O}_3$ , $\text{SiO}_2$ , $\text{MgO}$ , $\text{MnO}$ , $\text{CaO}$
not detected	$\text{Li}_2\text{O}$ , $\text{Cs}_2\text{O}$ , $\text{Rb}_2\text{O}$ .

The x-ray powder pattern agrees with that given in the original set of Diffraction Data Cards published by the American Society for Testing Materials. The index of refraction is  $1.910 \pm 0.002$ . Since yttria is very hygroscopic, the material was fired at  $1400^\circ$  for fifteen minutes before the measurement was made. The crystals are isometric and occur as rectangular plates.

## METHODS OF THERMAL INVESTIGATION

Because of the large range of temperature required and the necessity of maintaining the manganese in the manganous state, several different techniques were used to determine the equilibrium relationships. The method of suspending small portions of the prepared glass in a platinum packet or crucible in a nitrogen-atmosphere quenching furnace was employed for most of the charges with liquidus temperatures below  $1500^\circ$ . A few longer runs were made by sealing platinum packets containing the charges in evacuated silica glass tubes which could then be suspended in the resistance furnace without the otherwise necessary atmosphere of purified nitrogen. Temperatures were measured with a platinum vs. platinum-10 rhodium thermocouple calibrated at the melting points of gold and diopside,  $1062.6^\circ$  and  $1391.5^\circ$ , respectively, in accordance with the temperature scale used at the Geophysical Laboratory. In order to avoid contamination of the thermocouple, temperature readings were made only before and after a run, according to a fixed time schedule, the furnace temperature being held constant with a regulator of the Wheatstone bridge type (Roberts, 1941). Runs at temperatures between  $1500^\circ$  and  $1730^\circ$  were made in a Meker gas furnace in which a reducing atmosphere was maintained by adjustment of the gas to air ratio. Gas furnace temperatures were measured with an optical pyrometer. A fourth method, used for charges near the high-yttria end of the system, consists of placing a sintered disk of the charge in a molybdenum or iridium boat and heating for 1 to 5 minutes in a graphite-resistor vacuum furnace (Urry and Piggot, 1941). The temperature was determined approximately from a chart (power input vs. temperature) based on optical pyrometer measurements and on a calibration at the melting point of  $Al_2O_3$  ( $2050^\circ \pm 10^\circ$ ).

It is to be emphasized that the thermal investigation is of an exploratory nature. The temperatures of the runs, particularly the higher temperatures reported, are not precisely known and the composition of the mixtures is subject to several sources of error. For example, other oxides of manganese than manganous oxide are present in the glasses and sintered products even though the best available techniques were employed. In addition, some of the manganese is lost to the platinum container through alloying. This effect is reduced somewhat by using the same crucible for succeeding runs. Snow (1943) demonstrated that neither of those two sources of error is serious, although the index of refraction of the glasses is raised with increasing length of run. For example, the following changes of index of refraction were noted for the glass of spessartite composition:



<i>Present Work</i>	<i>Snow</i>
1 hr. $n=1.655$	1 hr. $n=1.666$
15 hrs. $n=1.662$	5 hrs. $n=1.671$

In general the loss of manganese lowers the index and an increase in  $\text{Mn}_2\text{O}_3$  raises the index. The color of the glass changes from colorless to brown with increasing length of run.

#### RESULTS OF THERMAL INVESTIGATION

Results of the determination of the phases at the various temperatures are given in Table 1. A preliminary temperature-composition diagram for the system  $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ , based on the data in Table 1, is given in Fig. 1. It was found that there is continuous solid solution between spessartite and yttrogarnet;<sup>2</sup> the liquidus near the end member  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$  is complicated by the existence of two crystalline forms having that composition. The liquidus temperature was obtained in the usual way by observing the presence or absence of crystals in quenched charges and the solidus was estimated from the proportion of glass to crystals in quenched charges from runs in the liquid + crystals region. Corroborative evidence for the position of the solidus was obtained from a plot of the change in unit-cell size of the crystals; the method of obtaining such evidence is described in a following section. The usual method of determining the solidus by observing the temperature at which crystallization is complete is not precise for the present study because films of glass about the crystals are easily overlooked. For this reason no great effort was made to fix the solidus precisely by thermal runs in this preliminary investigation. The dashed portions of the curves represent estimates of the equilibrium relations thought to exist in that region.

Equipment was not available to determine precisely either the transition from yttrogarnet to yttroalumite or the melting point of yttroalumite. The best estimate of the transition is  $1970^\circ \pm 50^\circ$  and of the melting point of yttroalumite,  $2110^\circ \pm 70^\circ$ . The reversible transformation between yttrogarnet and yttroalumite takes place in the solid state. The compound  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$  has not been synthesized previously. The synthesis of  $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  and  $3\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  have been reported (Goldschmidt, Barth, and Lunde, 1925, p. 33), but the system  $\text{Y}_2\text{O}_3 - \text{Al}_2\text{O}_3$  has not been studied completely.

<sup>2</sup> The name yttrogarnet is proposed for the low form of  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ . Yttrium-bearing garnets have been called yttrium garnet, yttriferous garnet, emildine, erinadine, yttergarnet, yttriogarnet, and yttrogarnet. The last name is in accord with the present system of nomenclature and adequately describes the compound  $\text{Y}_3\text{Al}_2(\text{AlO}_4)_3$ . The members of the series may be referred to as yttrian spessartites after Jaffe. The name yttroalumite is proposed for the high form of  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ .

TABLE 1

Composition				Initial condition	t° C.	Time	Phases present (per cent)	n glass	n crystal	d <sub>642</sub> crystal	
MnO	Y <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>								
43.00	—	20.60	36.40	glass	1080	18 hrs	garnet	—	1.800	1.557	
				glass	1180	15 hrs	garnet (95)+glass	n. d.	1.800	1.557	
				glass	1193	30 min	garnet (rare)+glass	1.653	n. d.	n. d.	
				glass	1196	30 min	glass	1.653	—	—	
				glass	1200	30 min	glass	1.655	—	—	
				powder	1216	1 hr	glass	1.655	—	—	
				powder	1218	15 hrs	glass	1.662	—	—	
powder	1256	15 hrs	glass	1.668	—	—					
*40.63	3.00	21.78	34.59	glass	1177	17 hrs	garnet+glass (rare)	n. d.	1.801	1.560	
				powder	1306	15 hrs	glass	1.663	—	—	
*38.70	5.88	22.66	32.76	glass	1202	15 hrs	garnet	—	1.801	1.564	
				powder	1269	22 hrs	garnet (10)+glass	1.663	1.805	1.575	
				powder	1317	2 hrs	glass	1.660	—	—	
36.30	8.89	24.08	30.73	glass	1247	1 hr	garnet (50)+glass	1.660	1.805	1.571	
				glass	1250	15 hrs	garnet (50)+glass	1.661	1.803	1.571	
				glass	1290	30 min	garnet (10)+glass	1.665	n. d.	1.576	
				powder	1329	19 hrs	garnet (rare)+glass	1.662	n. d.	n. d.	
				glass	1335	1 hr	glass	1.665	—	—	
				garnet+glass	1340	3 hrs	glass	1.669	—	—	
				glass	1439	5 min	glass	1.666	—	—	
32.25	14.27	26.18	27.30	glass	1273	1 hr	garnet (90)+glass	1.667	1.807	1.577	
				glass	1364	1 hr	garnet (10)+glass	1.671	1.810	1.589	
				powder	1446	16 hrs	glass	1.670	—	—	
25.80	22.83	29.53	21.84	pellet	1334	10 hrs	garnet (80)+glass	1.658	1.812	1.587	
				powder	1499	5 hrs	garnet (5)+glass	1.683	1.816	1.598	
				powder	1550	5 min	glass	1.682	—	—	
17.20	34.24	34.00	14.56	garnet+glass	1451	1 hr	garnet (95)+glass	1.667	1.818	1.597	
				glass	1498	1 hr	garnet (95)+glass	1.672	1.816	1.598	
				glass	1600	15 min	garnet (90)+glass	1.680	1.821	1.600	
				glass	1640	30 min	garnet (80)+glass	1.682	n. d.	n. d.	
				pellet	1720	1 hr	glass	n. d.	—	—	
				pellet	1730	10 min	glass	1.694	—	—	
—	57.07	42.93	—	pellet	1650	2 hrs	garnet	—	1.823	1.605	
					1730	1 hr					
				yttroalumite	1970	2 min	garnet+residual yttroalumite (few)	—	1.823	1.608	
					1970	5 min					
				garnet	1970	5 min	garnet	—	1.824	1.608	
				pellet	1970	5 min	garnet	—	1.823	1.608	
				yttroalumite	2020	5 min	residual yttroalumite (90)+garnet	—	see text		
				pellet	2040	5 min	garnet (probably poor quench)	—	1.823	1.608	
					2160	2 min					
				garnet	2160	2 min	melted: yttroalumite (99)+residual garnet	—	see text		
				pellet	2170	2 min	melted: garnet+ yttroalumite (rare)	—	1.823	1.608	
					2180	2 min					
				pellet	2180	2 min	melted: yttroalumite (99)+garnet	—	see text		
				garnet	2180	1 min	melted: yttroalumite (99)+garnet	—	see text		
				pellet	2180	5 min	melted: yttroalumite (95)+garnet	—	see text		

\* Composition slightly off join.

d<sub>642</sub>=spacing of plane 642 in Å

n=index of refraction

n. d.=not determined

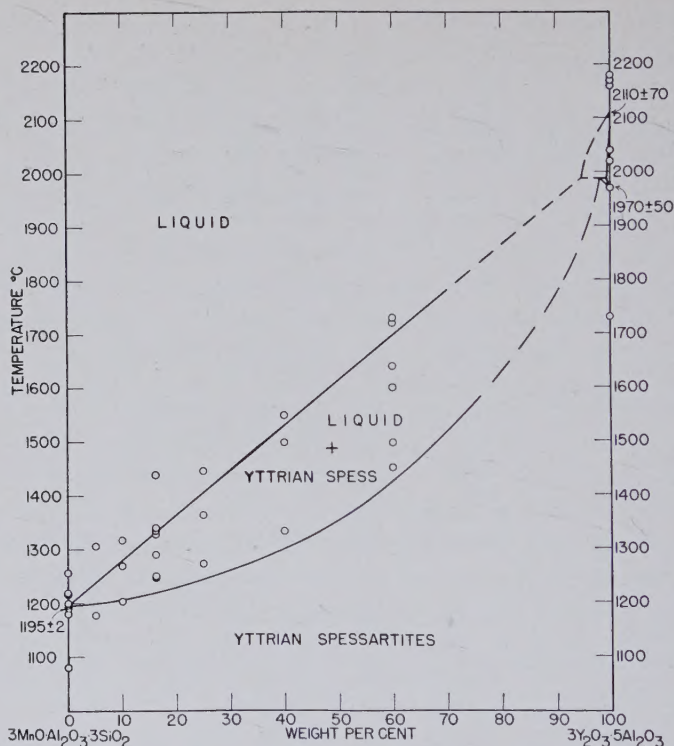


FIG. 1. Preliminary temperature-composition diagram for the system  $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ .

The melting point of spessartite crystallized from a glass having an index of refraction of 1.655 was found to be  $1195^\circ \pm 2^\circ$ . Spessartite has been synthesized by Gorgeu (1883), Menzer (1929), and Snow (1943). Snow determined the melting point of spessartite to be  $1200^\circ \pm 5^\circ$ ; however, his analysis indicates that the mix was slightly off composition. (The theoretical composition for spessartite is also given incorrectly.) In view of the experimental difficulties the agreement is considered to be good.

#### OPTICAL DATA

The index of refraction of the glasses in some of the quenched charges in the system  $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$  is given in Table 1 and plotted in Fig. 2. The index of refraction of the glasses from the shortest runs which quenched to glass only is represented by circles and used to construct the curve. The dots represent the index of refraction of glasses obtained from runs in the liquid + crystals region. By using



the curve in Fig. 2, the composition of the liquid phase for each experiment may be approximated and compared with the composition determined by the temperature method of fixing the liquidus (see Bowen, 1913, p. 585). The poor agreement obtained was to be expected because of the fact that the index of refraction of the glasses changes with increasing length of run.

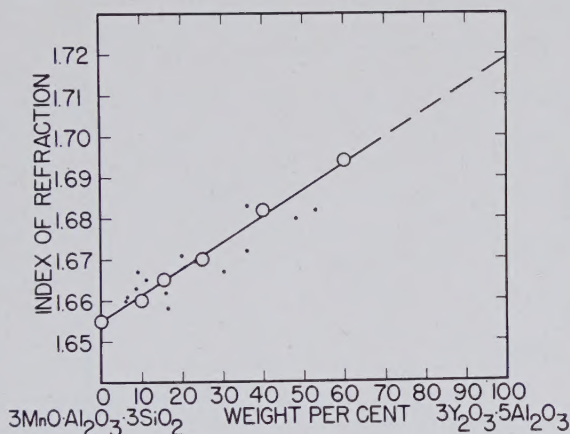


FIG. 2. Index of refraction of glasses in the system  $3MnO \cdot Al_2O_3 \cdot 3SiO_2 - 3Y_2O_3 \cdot 5Al_2O_3$ .

It was not possible to quench  $3Y_2O_3 \cdot 5Al_2O_3$  to a glass with the equipment at hand; therefore, the index of refraction of that glass is obtained by extrapolation of the curve in Fig. 2. The index of refraction of the  $3Y_2O_3 \cdot 5Al_2O_3$  glass is estimated to be 1.719. From the Gladstone and Dale relation (Larsen and Berman, 1934, p. 30) and using  $k_{Y_2O_3} = 0.176$ , determined in the present investigation, and  $k_{Al_2O_3} = 0.193$ , the density of the glass is calculated to be 3.92 as compared with a calculated density of 4.12 for its high temperature crystalline equivalent yttrioalumite. If Larsen and Berman's value of  $k_{Y_2O_3} = 0.144$  is used, the density of the glass is calculated to be higher than that of yttrioalumite.

The index of refraction of the garnet crystals obtained is given in Table 1 and presented in Fig. 3. Reference liquids having high indices of refraction were obtained from Dr. Esper S. Larsen, Jr. and Miss Sarah C. Johnson of the U. S. Geological Survey, and from Mr. Howard W. Jaffe of the U. S. Bureau of Mines. The liquids obtained through the courtesy of Dr. Larsen are almost colorless ( $n = 1.801-1.998$ ); they were calibrated by the minimum deviation method. The index of refraction of some of the reference liquids was measured by H. W. Jaffe on a Leitz-Jelley Microrefractometer at the same time as the measurement

of the index of refraction of the crystal was being made. Within the error of measurement ( $\pm 0.003$ ) the index of refraction of the garnet crystals indicates that there is continuous solid solution between spessartite and yttrigarnet. The deviations are probably due largely to errors in the determination of the composition of the crystals, and it is assumed, therefore, that the change of index of refraction from spessartite to yttrigarnet is essentially linear.

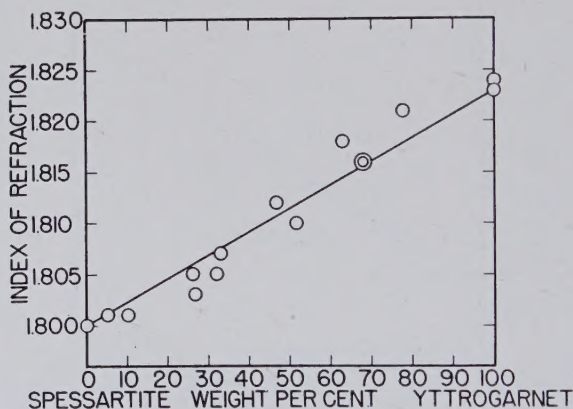


FIG. 3. Index of refraction of garnets in the system spessartite-yttrigarnet.

*Spessartite.* Spessartite crystallizes into irregular, light green grains up to 10 microns in diameter. Rare well-formed crystals were developed and these appeared as dodecahedrons. The crystals are isotropic and have an index of refraction of  $1.800 \pm 0.003$ . This agrees exactly with the index of refraction of 1.800 predicted for the pure compound by Ford (1915, p. 37). Snow gave a value of  $1.810 \pm 0.005$  for a synthetic spessartite which may not have been of the proper composition.

*Yttrigarnet.* These crystals were observed as rounded, light green, isotropic grains approximately one to five microns in diameter. Only a few dodecahedral crystals were observed. The index of refraction was found to be  $1.823 \pm 0.003$ .

*Yttrioalumite.* The high form of  $3Y_2O_3 \cdot 5Al_2O_3$  was observed as rounded, tabular crystals up to five microns in size. Most grains were observed to have biaxial negative figures, extinction inclined to the elongation, and  $n_{\max} = 1.942$ ,  $n_{\min} = 1.927$ . One grain gave a uniaxial negative figure. The x-ray data indicate that yttrioalumite is tetragonal, and therefore the biaxial figures are anomalous. It is noteworthy that the high-temperature form of  $3Y_2O_3 \cdot 5Al_2O_3$  has lower symmetry than the low-temperature form and has indices of refraction greater than those of its component oxides.



Two values of the specific refractivity of  $Y_2O_3$  were obtained from the Gladstone and Dale relation, using the following data:

	$n$ (measured)	$\rho$ (calculated from x-ray data)	$k$ (calculated specific refractivity for $Y_2O_3$ )
Yttrogarnet	1.823	4.55	0.172
Yttria	1.910	5.04	0.180
		mean	0.176

where  $n$  = index of refraction,  $\rho$  = density, and  $k_{Al_2O_3} = 0.193$  (Larsen and Berman, 1934, p. 31). The calculated mean refractive index of yttrioalumite, using  $\rho = 4.12$ ,  $k_{Y_2O_3} = 0.176$ , and  $k_{Al_2O_3} = 0.193$ , was found to be 1.755, which is considerably below the observed mean refractive index (1.934). Either the Gladstone and Dale relation does not hold in this case or the measured indices of refraction are anomalous.

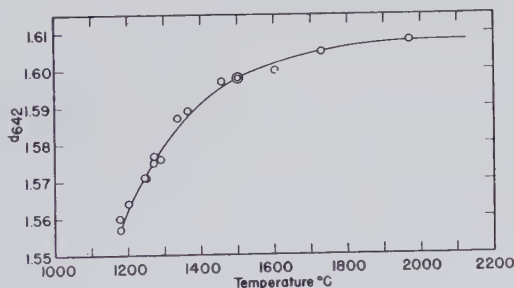


FIG. 4. Change of spacing,  $d$ , of the plane 642 in garnet crystals in the system spessartite-yttrogarnet with temperature of formation.

#### X-RAY DIFFRACTION DATA

Powder patterns were obtained for the products of all runs below the liquidus (see Table 1). A plot of  $d_{642}$  as a function of the temperature of formation of crystals in equilibrium with liquid is given in Fig. 4. The curve is essentially a reproduction of the solidus. Because there were not in all cases sufficient crystals present in the glass to give a good pattern, it was necessary to choose arbitrarily a prominent peak to indicate the change of unit-cell dimension. (In the isometric system the spacing of all planes is proportional to  $a_0$ .) The continuous nature of the change in unit-cell size with change in composition (see Fig. 5), in addition to the regular change in intensities, indicates that spessartite and yttrogarnet are isostructural. Regular positive deviations from Vegard's Law (Vegard, 1921) are not uncommon and in the present case may be due in part to the manner in which the composition of the crystals was

fixed by the location of the solidus. If Vegard's Law were assumed to be exactly satisfied, that is, if the unit-cell parameter varied linearly with composition expressed in atomic per cent, the solidus would be more convex toward the yttrogarnet composition. That being the case, estimated compositions of crystals would be higher in the yttrogarnet end member. Had other methods been lacking, the solidus could have been fixed approximately by applying Vegard's Law.

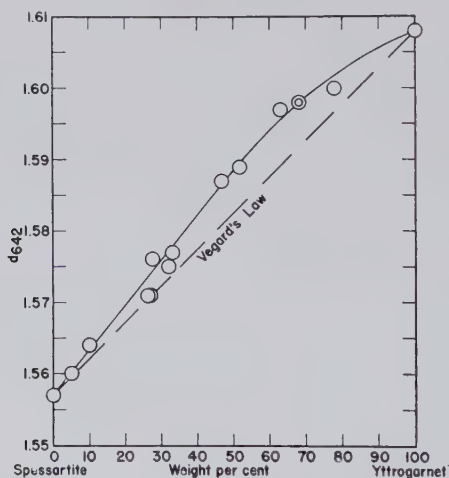


FIG. 5. Change of spacing,  $d$ , of the plane 642 in garnet crystals in the system spessartite-yttrogarnet with composition.

The cell edge for spessartite, space group  $O_h^{10}-Ia\bar{3}d$ , is  $11.63 \pm 0.02$  Å, and for yttrogarnet it is  $12.01 \pm 0.02$  Å. The intensities of the recorded reflections are given in Table 2. The observed intensities were taken to be proportional to the heights of the peaks on the graph from the Norelco  $x$ -ray spectrometer, and the height of the peak from the 420 plane was assigned the value 10. The increase in cell edge from spessartite to yttrogarnet was expected from the change of ionic radii;  $Mn_{VIII}^{+2} = 0.82$  Å is replaced by  $Y_{VIII}^{+3} = 0.96$  Å, and  $Si_{IV}^{+4} = 0.39$  Å is replaced by  $Al_{IV}^{+3} = 0.47$  Å (radii from Pauling, 1945).<sup>3</sup> The cell edge of grossularite,  $Ca_3Al_2(SiO_4)_3$ , whose structure was determined by Menzer (1929), is 11.864 Å. Here  $Ca_{VIII}^{+2} = 1.02$  Å is replaced by  $Y_{VIII}^{+3} = 0.96$  Å; the change in spacing apparently is more than counteracted by the difference in Si and Al radii.

To test the isostructural character of grossularite, spessartite, and yttrogarnet, the intensities were calculated using as a first approximation the coordinates given by Menzer for grossularite (Table 3).

<sup>3</sup> The superscripts indicate the valence; the subscripts, the coordination number.



TABLE 2

Grossularite Georgetown, California					Spessartite (synthetic)				Yttrogarnet (synthetic)			
$C_h^{10}$ $hkl$	$d$ Calc.	$d$ Obs.	$I^*$ Calc.	$I$ Obs.	$d$ Calc.	$d$ Obs.	$I^*$ Calc.	$I$ Obs.	$d$ Calc.	$d$ Obs.	$I^*$ Calc.	$I$ Obs.
211	4.84	N.O.	0.16	—	4.75	4.76	0.74	0.5	4.90	4.89	2.49	3.5
220	4.19	N.O.	0.11	—	4.11	N.O.	0.00	—	4.25	4.24	0.38	1
321	3.17	N.O.	0.25	—	3.11	3.10	0.80	0.7	3.21	3.21	2.19	2
400	2.96	2.96	3.59	4.5	2.91	2.91	3.06	2.5	3.00	3.00	2.37	3
420	2.65	2.65	10.00	10	2.60	2.60	10.00	10	2.69	2.69	10.00	10
332	2.53	2.53	0.95	1	2.48	2.48	0.32	1	2.56	N.O.	0.00	—
422	2.42	2.42	2.50	2.5	2.37	2.37	2.40	1.5	2.45	2.45	2.24	2.5
431	2.32	2.33	1.57	3	2.28	2.28	1.09	1	2.36	2.36	0.55	0.5
521	2.16	2.16	1.61	2	2.12	2.13	1.71	1.5	2.19	2.19	2.18	3
440	2.09	2.10	0.36	0.5	2.06	2.06	0.41	0.5	2.12	2.13	0.47	0.5
611	1.922	1.920	1.40	4	1.887	1.886	1.26	2	1.948	1.952	1.30	3
532			1.14				2.38				1.58	
620	1.874	1.879	0.00	0.5	1.839	1.836	0.01	0.2	1.899	N.O.	0.15	—
541	1.828	N.O.	0.03	—	1.794	1.797	0.02	0.2	1.853	N.O.	0.01	—
631	1.747	N.O.	0.13	—	1.715	1.710	0.02	0.2	1.771	1.772	0.11	0.2
444	1.710	1.713	1.40	2	1.679	1.681	1.41	2	1.734	1.734	1.70	2.5
543	1.676	1.678	0.27	0.5	1.645	1.650	0.18	0.5	1.698	N.O.	0.09	—
640	1.643	1.647	3.49	4	1.613	1.614	3.11	3	1.666	1.666	3.11	4
721	1.613	1.616	0.01	0.5	1.583	1.586	0.04	0.5	1.634	1.635	0.28	1
633			0.00				0.01				0.11	
552			0.14				0.16				0.31	
642	1.583	1.586	4.56	5	1.554	1.557	3.71	4	1.605	1.608	2.84	3.5
732	1.505	N.O.	0.01	—	1.477	1.482	0.00	0.2	1.525	1.528	0.15	0.5
651			0.00				0.03				0.33	
800	1.481	1.485	1.18	1	1.454	1.456	1.09	1.5	1.501	1.503	1.12	1.5
$a_0$	$11.85 \pm 0.01 \text{ \AA}$				$11.63 \pm 0.02 \text{ \AA}$				$12.01 \pm 0.02 \text{ \AA}$			
$\rho$ calc.	3.595				4.179				4.552			
$\rho$ obs.	3.53				>4.0				>4.0			
$n$	$1.736 \pm 0.001$				$1.800 \pm 0.003$				$1.823 \pm 0.003$			
$z$	8				8				8			

\* $I$  = Intensity;  $I_{400} = 10$  $\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$  $z$  = Number of formula weights per unit cell $d$  = spacing of planes in  $\text{\AA}$ 

N.O. = Not Observed

Nickel Filter

 $\rho$  = density

Norelco X-ray Spectrometer

 $n$  = Index of Refraction

Intensities were calculated for 25 reflections by means of the formula:

$$I \propto |F|^2 m \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

where  $F$  is the structure factor,  $m$  the multiplicity factor, and  $\theta$  the glancing angle. The calculations were made using James and Brindley's values

TABLE 3

Grossularite	Spessartite	Yttrogarnet	Atomic positions			
Ca <sup>+2</sup>	Mn <sup>+2</sup>	Y <sup>+3</sup>	24(c)	$\frac{1}{4}$	$\frac{1}{8}$	0
Al <sup>+3</sup>	Al <sup>+3</sup>	Al <sup>+3</sup>	16(a)	0	0	0
Si <sup>+4</sup>	Si <sup>+4</sup>	Al <sup>+3</sup>	24(d)	$\frac{1}{4}$	$\frac{3}{8}$	0
O <sup>-2</sup>	O <sup>-2</sup>	O <sup>-2</sup>	96(h)	$x=0.04$		
				$y=0.055$		
				$z=0.64$		

for the scattering powers of the ions as given in the Internationale Tabellen. Scattering factors for Y<sup>+3</sup> and Mn<sup>+2</sup> were obtained by graphical approximation; the following values were used:

$10^{-8}x \sin \theta/\lambda$	0.0	0.1	0.2	0.3	0.4	0.5	0.6
$f_0 - Y^{+3}$	36.0	33.8	30.1	26.1	22.7	20.0	17.8
$f_0 - Mn^{+2}$	23.0	21.3	18.2	14.6	12.3	10.8	9.7

Results of the calculations are given in Table 2.<sup>4</sup> It can be seen on inspection that the agreement of the observed intensities to the calculated intensities is very good.<sup>5</sup> It is concluded that the assumed structures are essentially correct.

Pauling's electrostatic bond rule is completely satisfied in each case. In intermediate compositions, the positions 24(c) and 24(d) comprise variate atom equipoints (Barth and Posnjak, 1931).

A study of a solid model of Menzer's grossularite structure shows that Ca is surrounded by eight nearly equidistant oxygens. Within the stated limits of error, the Ca-O distances are indistinguishable. Menzer gives Ca-O =  $2.46 \pm 0.20$  Å for four distances and Ca-O =  $2.36 \pm 0.13$  Å for the other four. The oxygens about the calcium form a hexahedron which in this case is a greatly distorted cube. Eight-fold coordination is common for Ca<sup>+2</sup>, but it is unusual for Mg<sup>+2</sup>, Fe<sup>+2</sup>, and Mn<sup>+2</sup> which replace Ca<sup>+2</sup>. More precise data are needed to ascertain the bond lengths in these structures.

<sup>4</sup> The calculations for grossularite have been made previously by Pabst (1937, p. 863; 1942, p. 790). The agreement is good when account is taken of the differences in radiation and the discrepancies resulting from differences in interpolation of the scattering, Lorentz and polarization factors. Dr. Pabst kindly located several errors in the preliminary calculations.

<sup>5</sup> The discrepancy factor  $\sum ||F_{obs.}| - |F_{calc.}|| / \sum |F_{obs.}| = 0.14$  compares favorably with previous factors reported in the literature. It has been suggested that regression analysis (see for example Snedecor, 1946, pp. 103-137) of the data would provide a more meaningful test. Perfect agreement between  $I_{obs}$  and  $I_{calc}$  would generate regression and correlation coefficients equal to unity. For the yttrogarnet data the regression coefficient is 1.19, with an error of 0.086, and the correlation coefficient is 0.959. According to the conventional statistical interpretation, the assumed structure thus accounts satisfactorily for the observations.



Within the knowledge of the writers, yttrigarnet and  $\gamma$ - $Al_2O_3$  are the only examples on record of structures in which silicon is absent, possessing aluminum in two coordinations. Yttrigarnet is also an example of a rare combination involving metal atoms each of which has three positive charges.

The powder diffraction data for yttrioalumite are given in Table 4. A preliminary study by Dr. Gabrielle Donnay indicates a tetragonal cell with  $a=7.51$  Å,  $c=4.24$  Å, and one formula weight per cell giving  $\rho_{calc.}=4.12$ . The lattice is primitive; no systematic absences are found.

TABLE 4. POWDER X-RAY DIFFRACTION DATA FOR SYNTHETIC YTTRIOALUMITE\*

$d$ in Å	$I/I_0 \times 10$	$d$ in Å	$I/I_0 \times 10$
4.24	0.5	1.694	0.2
3.70	4.5	1.655	1.0
3.68	4.0	1.640	2.5
3.36	2.5	1.605	1.0
3.32	2.0	1.531	1.5
2.89	0.3	1.519	1.5
2.67	4.0	1.503	4.5
2.62	10.0	1.485	0.5
2.59	3.0	1.389	1.0
2.51	2.5	1.312	2.0
2.26	0.3	1.296	0.5
2.22	1.5	1.243	0.5
2.16	2.5	1.229	0.5
2.12	2.0	1.224	1.0
2.05	1.5	1.194	0.1
1.996	0.3	1.187	0.3
1.972	0.3	1.173	3.0
1.859	4.0	1.170	3.0
1.845	3.0	1.159	0.5
1.806	2.0	1.154	1.0

\*  $CuK_{\alpha}$  radiation, Nickel filter, Norelco X-ray Spectrometer.

## DISCUSSION

The importance of the synthesis and structural identification of the yttrigarnet is twofold. It demonstrates one of the ways in which yttrium may enter the garnet structure. It should be clear that this is not the only way in which yttrium might go into the garnet structure. Jaffe (1950), in his discussion of the yttrian garnet from Iisaka (Iizaka), Japan, suggests that  $Na^{+1}Y^{+3} \rightarrow 2Mn^{+2}$ . In this case the sodium and yttrium atoms would be distributed randomly over the  $24(c)$  position

and would cause little distortion of the structure. Rankama and Sahama (1950, p. 526) suggest that yttrium goes into garnet in another manner which the present writers interpret as follows:  $Y^{+3}Mg^{+2} \rightarrow Mn^{+2}Al^{+3}$ . Magnesium is about the only atom with a valence of two which has the requisite radius that could substitute in the 16(a) position. The limiting end member in this substitution would be a compound of the composition  $(MnY_2)Mg_2(SiO_4)_3$ . In the past magnesium has been thought to enter the garnet structure only in the 24(c) position, as in pyrope.

The series spessartite-yttrogarnet is, in addition, the first example of an orthosilicate in which the substitution of aluminum for silicon can be carried to completion. It contradicts the prevalent idea that the substitution of aluminum for silicon always decreases as the Si/O ratio decreases. That concept has been presented by Machatschki (1928), Warren (1930), Bragg (1930), and more specifically by de Jong (1935). The limits to which aluminum may substitute for silicon in the various linkages of tetrahedra are given by de Jong as follows:

SiO <sub>4</sub>	Orthosilicate group	none or little
Si <sub>2</sub> O <sub>7</sub>	Complex group	none or little
SiO <sub>3</sub>	Chain	$\frac{1}{4}$
Si <sub>4</sub> O <sub>11</sub>	Double chain	$\frac{1}{2}$
Si <sub>2</sub> O <sub>5</sub>	Sheet	$\frac{1}{4}$ to $\frac{1}{2}$
SiO <sub>2</sub>	Network	$\frac{1}{2}$

Although the complete substitution which has been experimentally demonstrated for an orthosilicate may be an exception, further study should be given to the general concept of the limits of aluminum substitution for silicon.

#### ACKNOWLEDGMENTS

Drs. Gabrielle Donnay and J. D. H. Donnay gave many helpful suggestions as well as instruction in the structure factor calculations. The continuing interest and stimulative discussions of Howard W. Jaffe are gratefully acknowledged.

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## NASONITE AND ITS RELATION TO PYROMORPHITE\*

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### ABSTRACT

Two new analyses of nasonite from Franklin, New Jersey, confirm the formula  $\text{Pb}_6\text{Ca}_4(\text{Si}_2\text{O}_7)_3\text{Cl}_2$ . A Weissenberg  $x$ -ray study gave  $a_0=10.06$  kX,  $c_0=13.24$ ,  $a_0:c_0=1:1.3161$ ; space group  $C6_3/m$  or  $C6_3$ ; cell contents  $\text{Pb}_{12}\text{Ca}_8(\text{Si}_2\text{O}_7)_6\text{Cl}_4$ . The very close analogy in composition and geometry between nasonite and pyromorphite,  $\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$ , is discussed.

Nasonite,  $\text{Pb}_6\text{Ca}_4(\text{Si}_2\text{O}_7)_3\text{Cl}_2$ , has been described from Franklin, New Jersey, by Penfield and Warren<sup>1</sup> and by Palache<sup>2</sup> and from Långban, Sweden, by Aminoff.<sup>3</sup> The mineral is extremely rare and few specimens are extant. Recently small amounts of the mineral have been found at Franklin below the 800 level in pillar 910 south of the Palmer shaft. The nasonite is associated with barysilite ( $\text{Pb}_3\text{Si}_2\text{O}_7$ ), granular datolite, white fibrous prehnite, willemite, axinite, hancockite, garnet, clinochlore, and manganophyllite. These minerals occur as irregular masses and indistinct veinlets cutting the franklinite-willemite ore and owe their formation to the local introduction of hydrothermal solutions carrying lead, boron and chlorine—all elements notably rare in the normal ore.

The nasonite occurs as white, granular masses with a greasy-adamantine luster. The mineral is not fluorescent. Minute prismatic crystals of the habit shown in Fig. 1 occur projecting into tiny cavities. Two new chemical analyses are cited in Table 1 together with the specific gravity and optical properties as newly measured. The indices of refraction are somewhat higher than those reported by Larsen on the material described by Palache. The analyses conform to the formula  $\text{Pb}_6\text{Ca}_4(\text{Si}_2\text{O}_7)_3\text{Cl}_2$ . A small amount of  $\text{Mn}''$  substitutes for Pb in the material of analysis 1. The mineral ganomalite,  $\text{Pb}_6\text{Ca}_4(\text{Si}_2\text{O}_7)_3(\text{OH})_2$ , is isostructural with nasonite but the reported analyses of this species<sup>4</sup> and of nasonite show only a slight mutual substitution of Cl and OH.

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 328.

<sup>1</sup> Penfield, S. L., and Warren, C. H., *Am. J. Sci.*, **8**, 339 (1899).

<sup>2</sup> Palache, C., *U. S. Geol. Surv., Prof. Paper* **180**, 92 (1935).

<sup>3</sup> Aminoff, G., *Geol. För. Förh.*, **38**, 473 (1916).

<sup>4</sup> Flink, G., *Arkiv Kemi, Min., Geol.*, **6**, no. 21, 16 (1917), and Dana, E. S., *System of Mineralogy*, 6th ed., 422 (1892).

TABLE 1. ANALYSES OF NASONITE

	1	2	3
CaO	10.98	10.92	11.34
MgO	—	0.24	
MnO	2.37	0.63	
PbO	65.96	66.48	67.68
ZnO	0.03	—	
SiO <sub>2</sub>	18.32	18.57	18.21
Cl	3.07	3.18	3.58
H <sub>2</sub> O+	0.25	0.29	
	100.98	100.31	100.81
O=Cl	0.69	0.72	0.81
Total	100.29	99.59	100.00
G		5.55	
nO	1.946 (Na)	1.946 (Na)	
nE		1.969	

1. Nasonite. Franklin, N. J. Associated with barysilite, Bauer analysis, 1950.
2. Nasonite. Franklin, N. J. Associated with hancockite, datolite, garnet. Bauer analysis, 1950.
3.  $\text{Pb}_6\text{Ca}_4(\text{Si}_2\text{O}_7)_3\text{Cl}_2$ . Theoretical composition.

A Weissenberg x-ray study of crystals from the material of analysis 2 gave:

$$\begin{aligned}
 a_0 &= 10.06 \text{ kX} & a_0:c_0 &= 1:1.3161 \\
 c_0 &= 13.24 & a:c &= 1:1.317 \text{ (Palache; morphology)} \\
 & \text{Space group } C6_3/m \text{ or } C6_3. \\
 & \text{Cell contents } \text{Pb}_{12}\text{Ca}_8(\text{Si}_2\text{O}_7)_6\text{Cl}_4 \\
 & \text{Calculated specific gravity } 5.63.
 \end{aligned}$$

The morphological study of Palache showed the mineral to be hexagonal and not tetragonal as originally thought by Penfield and Warren. His crystals were prismatic  $\{10\bar{1}0\}$ ,  $\{11\bar{2}0\}$  with  $\{10\bar{1}1\}$  as the only terminal form. The present crystals, like those from Långban described by Aminoff, are terminated by a large face of  $\{0001\}$ . Doubly terminated crystals are not known. The available morphological data does not permit the crystal class to be fixed within the Laue centro-symmetrical group  $6/m$  established by x-ray study. A decisive test for the presence or absence of piezoelectricity could not be obtained.

Nasonite shows an interesting dimensional and chemical relation to the members of the apatite group. A comparison of nasonite and pyromorphite is given in Table 2.



Nasonite is not an isotype of pyromorphite in the sense that  $\text{Zr}(\text{SiO}_4)$  and  $\text{Y}(\text{PO}_4)$  or  $\text{CaTi}(\text{SiO}_4)\text{O}$  and  $\text{CaMg}(\text{AsO}_4)\text{F}$  are isotypes. In nasonite the Si:O ratio is 2:7 implying the existence of  $(\text{Si}_2\text{O}_7)$  groups, whereas the structure of the members of the apatite group is based on isolated tetrahedral anions  $(\text{ZO}_4)$ , where Z is  $\text{P}^5$ ,  $\text{As}^5$  or  $\text{V}^5$  ordinarily, and sometimes in part  $\text{S}^6$ ,  $\text{Si}^4$  or  $\text{C}^4$ . The Z:O ratio always appears to be 1:4 in compounds of the apatite structure-type, including the silician and

TABLE 2. COMPARISON OF NASONITE AND PYROMORPHITE

	Nasonite	Pyromorphite
Formula	$\text{Pb}_6\text{Ca}_4(\text{Si}_2\text{O}_7)_3\text{Cl}_2$	$\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$
Space group	$C6_3/m$ or $C6_3$	$C6_3/m$
$a_0$	10.06 kX	9.95 kX
$c_0$	13.24	7.31 ( $\times 2 = 14.62$ )
$a_0:c_0$	1:1.3161	1:0.735
$\rho$ for $\{h0\bar{h}1\}$	$56^\circ 40'$ $p\{10\bar{1}1\}$	$59^\circ 32'$ $y\{20\bar{2}1\}$
G	5.55	7.04
H	4	$3\frac{1}{2}-4$
$n_O$	1.946 (Na)	2.058 (Na)
$n_E$	1.969	2.048
Sign	+	—

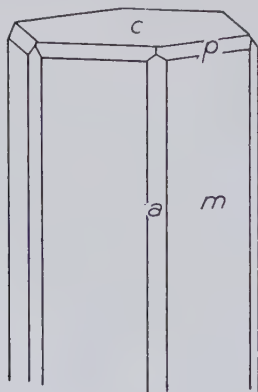


FIG. 1. Nasonite.

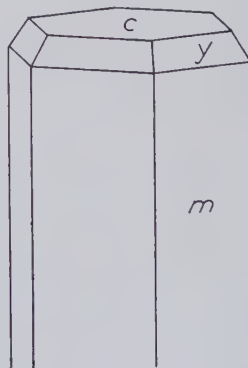


FIG. 2. Pyromorphite.

sulfatian members such as ellestadite, wilkeite and artificial  $\text{Ca}_{10}\text{Si}_2\text{P}_2\text{S}_2\text{O}_{24}\text{F}_2$ . The serial substitution of  $\text{Si}^4$  for  $\text{P}^5$  in apatite-type substances appears from the analytical evidence to be balanced electrostatically by a concomitant serial substitution such as of  $\text{S}^6$  for  $\text{P}^5$  or of  $\text{Na}^1$  for  $\text{Ca}^2$  with maintenance of the ratio Z:O = 1:4. The broad similarity between nasonite and pyromorphite presumably follows from a near equivalence

in the geometrical manner of packing of  $3(\text{Si}_2\text{O}_7)^{-6} = 6(\text{PO}_4)^{-3}$  with equal numbers of Cl and (Pb, Ca) ions.

The members of the apatite group diverge in symmetry and dimensions even more widely from silicates of the formula-type  $\text{A}_4''\text{B}_6'''(\text{SiO}_4)_6(\text{OH})_2$ . These silicates comprise the orthorhombic species zoisite and the monoclinic species clinozoisite, epidote, allanite and hancockite, where A is Ca chiefly with minor Pb, Sr, Ce or  $\text{Mn}''$  and B is Al chiefly with minor  $\text{Fe}'''$  or  $\text{Mn}'''$ . The formulation of the epidote group as nesosilicates, however, may be in error since Ito<sup>5</sup> recently has derived a structure for epidote based on chain-linkages of the  $(\text{SiO}_4)$  tetrahedra rather than on isolated  $(\text{SiO}_4)$  groups.

The only other formula-types among nesosilicates that contain a total of 10 cations together with  $6(\text{SiO}_4)$  groups and  $2(\text{OH})$ , and hence might afford crystals isotypic with apatite, are the following:  $\text{B}_8''' \text{C}_2'(\text{SiO}_4)_6(\text{OH})_2$ ,  $\text{A}_2'' \text{B}_7''' \text{C}'(\text{SiO}_4)_6(\text{OH})_2$ ,  $\text{A}_7'' \text{D}_3'''(\text{SiO}_4)_6(\text{OH})_2$ ,  $\text{A}'' \text{C}_4' \text{D}_5'''(\text{SiO}_4)_6(\text{OH})_2$ ,  $\text{A}_4'' \text{C}_2' \text{D}_4'''(\text{SiO}_4)_6(\text{OH})_2$ ,  $\text{B}_2''' \text{C}_4' \text{D}_4'''(\text{SiO}_4)_6(\text{OH})_2$  and  $\text{A}_5'' \text{B}_4''' \text{D}'''(\text{SiO}_4)_6(\text{OH})_2$ . Actual silicates belonging to these formula-types are not known. In any case, it is unlikely that an isotypic relation would exist with silicates containing cations of valence of three or greater since the small size and relatively highly polarizing character of these would result in a coordination different from that of the relatively large divalent cations of the apatite structure-type.

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## ISOMORPHISM AND BOND TYPE

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Since the classical work of V. M. Goldschmidt on ionic radii and crystal structure, mineralogists have considered that a necessary and almost sufficient condition for two atoms to show mutual replacement, is that they should have similar ionic radii. In a recent paper on the geochemistry of zinc, Dr. H. Neumann (1) has drawn attention to the fact that magnesium and iron enter only to a limited extent minerals of zinc. As these three atoms have similar ionic radii and identical charge they would be expected to permit a large amount of mutual solid solution.

During the past few years studies on bond lengths, bond energies, etc., have indicated that, in general, a bond between unlike atoms cannot be described as being purely ionic or covalent, but will be some combination of the two extreme types, or will be a hybrid bond, resonating between the two extreme forms. It has also been recognized that even where ionic bonding predominates the partial covalent character of the bond may lead to a considerable shortening of interatomic distance and ionic radii have not been entirely additive. For this reason it has been necessary to construct tables of covalent as well as ionic radii. One of the classical differences between ionic and covalent bonding is that where ionic bonding predominates there are no special restrictions on the bonds and the radius ratio rule will apply; i.e. the structure will depend on the relative sizes of the cations and anions, while in structures where covalent bonding predominates the structure is largely determined by the directional properties of the bonds; e.g. the bonds in carbon compounds where the carbon atom always forms four bonds directed to the corners of a regular tetrahedron. It is thus of considerable interest to the mineralogist to know approximately what type of bond exists in particular minerals so that some idea of whether these restrictions of configuration will be present or not.

The extent to which atoms form ionic or covalent bonds depends largely on two factors. If the ionization potential is low it will require little energy to remove electrons and thus an atom with a low ionization potential will tend to form ionic bonds. Conversely if the ionization potential is high there will be little tendency to lose electrons. Again, if the electron affinity is high an atom will have a tendency to acquire electrons and form an ionic bond. The balance of these two factors, ionization potential and electron affinity, largely determines the character of a bond. Thus, cesium fluoride is one of the most ionic compounds



known because cesium has the lowest ionization potential of any element and a negligible electron affinity, while fluorine has a very high electron affinity and ionization potential. These two factors have been combined in what is known as the electronegativity of an atom. L. Pauling (2) from work on the dipole moments of the halogen hydrides has related the difference in electronegativity of atoms to the type of bond that will form between them (Fig. 1). It is thus possible to estimate approximately from the electronegativities of atoms the extent of covalent and ionic bonding. Probably the most reliable electronegativity values are those of Haissinsky (3).

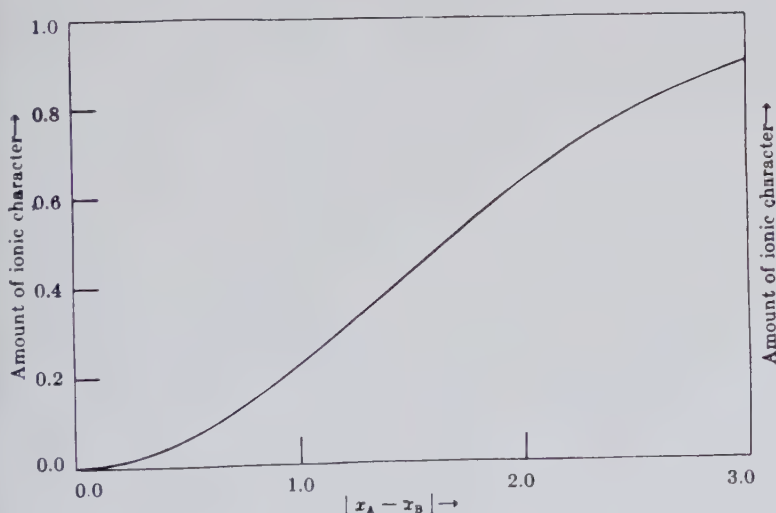


FIG. 1. Curve relating amount of ionic character of a bond A—B to the difference in electronegativity  $\chi_A - \chi_B$  of the atoms. (Reproduced by courtesy of L. Pauling.)

If covalent bonding predominates the configuration and coordination number of an atom will depend on the type of covalent bond formed, which in turn depends on the number and type of orbitals available for covalent bond formation. Thus, if a combination of one "s" and three "p" orbitals are available, four tetrahedrally directed bonds will occur. Again if two "d" one "s" and three "p" electrons are available an octahedral configuration will be assumed. The major types of possible hybridizations are summarized by Syrkin and Dyatkina (4). The situation is complicated further by the fact that when the covalent bonding is weak, resonance may occur leading to a larger number of bonds than there are available orbitals e.g. four tetrahedral bonds may resonate among six positions leading to an octahedral configuration (5).

It will now be of interest to consider the case of isomorphism in zinc,

TABLE 1. ELECTRONEGATIVITIES OF ELEMENTS

Element	Electro- negativity	Element	Electro- negativity
Hydrogen	2.1	Niobium	(1.6)
Lithium	1.0	Molybdenum <sup>4</sup>	(1.6)
Beryllium	1.5	Molybdenum <sup>5</sup>	(2.1)
Boron	2.0	Ruthenium	2.05
Carbon	2.5	Rhodium	2.1
Nitrogen	3.0	Palladium	2.0
Oxygen	3.5	Silver	1.8
Fluorine	4.0	Cadmium	1.5
Sodium	0.9	Indium	1.6
Magnesium	1.2	Tin <sup>2</sup>	1.65
Aluminium	1.5	Tin <sup>4</sup>	1.8
Silicon	1.8	Antimony <sup>3</sup>	1.8
Phosphorus	2.1	Antimony <sup>5</sup>	2.1
Sulfur	2.5	Tellurium	2.1
Chlorine	3.0	Iodine	2.6
Potassium	0.8	Cesium	0.7
Calcium	1.0	Barium	0.85
Scandium	1.3	Lanthanum	0.85
Titanium <sup>4</sup>	1.6	Cerium	1.05
Vanadium <sup>3</sup>	1.35	Praseodymium	1.1
Vanadium <sup>4</sup>	1.6	Hafnium	(1.3)
Vanadium <sup>5</sup>	1.8	Tantalum	(1.4)
Chromium <sup>2</sup>	1.5	Tungsten <sup>4</sup>	(1.6)
Chromium <sup>3</sup>	1.6	Tungsten <sup>6</sup>	2.1
Chromium <sup>6</sup>	(2.1)	Osmium	(2.1)
Manganese <sup>2</sup>	1.4	Iridium	2.1
Manganese <sup>3</sup>	(1.5)	Platinum	2.1
Manganese <sup>7</sup>	(2.3)	Gold	2.3
Iron <sup>2</sup>	1.65	Mercury <sup>1</sup>	1.8
Iron <sup>3</sup>	1.8	Mercury <sup>2</sup>	1.9
Cobalt	1.7	Thallium <sup>1</sup>	1.5
Nickel	1.7	Thallium <sup>3</sup>	1.9
Copper <sup>1</sup>	1.8	Lead <sup>2</sup>	1.6
Copper <sup>2</sup>	2.0	Lead <sup>4</sup>	1.8
Zinc	1.5	Bismuth	1.8
Gallium	1.6	Polonium	(2.0)
Germanium	1.7	85	(2.4)
Arsenic	2.0	87	0.7
Selenium	2.3	Radium	0.8
Bromine	2.8	Actinium	(1.0)
Rubidium	0.8	Thorium	1.1
Strontium	1.0	Proto Actinium	(1.4)
Yttrium	1.2	Uranium	1.3
Zirconium	1.4		

Values are taken from Haissinsky and Pauling.

Those in parentheses are only approximate.

manganese and iron minerals. Some of the binary compounds of these minerals are listed in Table 2 with the co-ordination numbers and approximate covalent character of the bonds.

TABLE 2. APPROXIMATE TYPE OF BOND IN BINARY COMPOUNDS OF ZINC, MAGNESIUM AND IRON

Non-Metal	Zinc		Magnesium		Iron	
	% Cov.	C.N.	% Cov.	C.N.	% Cov.	C.N.
Fluorine	23	6	14	6	27	6
Chlorine	57	6	45	6	65	6
Bromine		?	55	6	75	6
Iodine		?	60	6	80	6
Oxygen	37	4	28	6	43	6
Sulfur	78	4	67	6	84	6
Selenium	85	4	74	6	90	6
Tellurium	92	4	82	4	95	6
Silicon			90	4		
Germanium			90	4		
Tin			93	4		

On the basis of the electronic structures of these three elements it would be predicted that zinc and magnesium would most readily form tetrahedral hybrid bonds while iron would form octahedral bonds. In the compounds where covalent bonding predominates this is certainly the case. It will also be noticed that in compounds with more ionic character that zinc and magnesium are both octahedrally co-ordinated. This may be due to resonance of the four bonds among six positions. Zinc has a greater electronegativity than magnesium and hence zinc compounds are more covalent. Magnesium only assumes the co-ordination number four in extremely covalent structures. This may be due to the fact that magnesium has an eight electron shell inside its valence electrons while zinc has a shell of eighteen. In general metals with eight shells are reluctant to form covalent bonds unless they are of small size.

It would be expected that the fluorides and chlorides of these metals would be isomorphous, for in all these cases the configuration and size of the groups will be similar.

It is rather surprising that zinc in zinc oxide has a co-ordination number four in a compound of such ionic character. However, zinc and iron do enter into periclase to a marked extent, and zinc is also in six-co-ordination in its carbonate. It does appear in fact, that the zinc-oxygen bond is fairly near a transition point from tetrahedral to octahedral bonding. It is in this class of compound as Neumann points out that



most of the isomorphous replacement of zinc by iron and magnesium occurs.

Consideration of these conceptions suggests that the rules predicting isomorphism may require some extension. It appears that two atoms will be mutually replaceable in ionic compounds if their sizes are similar, and will be replaceable in more covalent compounds only if the number, and directional properties of their bonds, are similar.

Atoms of similar electronic structure and size should be isomorphous for they will form similar hybrid bonds. The transition metals do show a large amount of isomorphism and this would be expected from their similar sizes and the fact that they would all form octahedral hybrid covalent bonds. The alkali and alkaline earths also form a group for these are the most electropositive elements and the bonding in most of their minerals will be ionic and thus ionic radius will be the major governing factor. Zinc, cadmium and mercury all show some mutual solubility as would be expected. It thus appears that groups of the periodic table with similar structures do show some mutual solubility where the sizes are not too different.

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# COMPUTATION OF THE OPTIC AXIAL ANGLE FROM THE THREE PRINCIPAL REFRACTIVE INDICES

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## ABSTRACT

The standard equation for computing the value of the optic axial angle,  $2V_\gamma$ , of a biaxial crystal from its three principal refractive indices,  $\alpha$ ,  $\beta$ ,  $\gamma$ , is:  $\tan^2 V_\gamma = (1/\alpha^2 - 1/\beta^2)/(1/\beta^2 - 1/\gamma^2)$ . This equation is not in convenient form for use in computation. However, an approximate equation,  $\cos 2V_\gamma = (\epsilon - \delta)/(\epsilon + \delta) - 6\epsilon\delta/(\epsilon + \delta)(\gamma + \alpha)$ , in which  $\epsilon = \gamma - \beta$ ,  $\delta = \beta - \alpha$ , can be derived from it which is satisfactory and yields values accurate, in general, to 1' of arc for  $2V_\gamma$ , if the birefringence,  $\gamma - \alpha$ , does not exceed 0.050; and to 3' of arc in case  $\gamma - \alpha$  is between 0.050 and 0.100. The simplified formula shows clearly that the optic axial angle is primarily dependent on the difference between the partial birefringences,  $\gamma - \beta$ , and  $\beta - \alpha$ , divided by the maximum birefringence,  $\gamma - \alpha$ , rather than upon the actual values of  $\alpha$ ,  $\beta$ ,  $\gamma$ . The size of the index ellipsoid itself depends upon the values of the principal refractive indices; its shape, on the other hand, depends upon relations between the principal birefringences.

The optical properties of non-opaque biaxial crystals are most readily deduced from the index ellipsoid in which the three principal axes are the refractive indices,  $\alpha$ ,  $\beta$ ,  $\gamma$ , in ascending order of magnitude. In any triaxial ellipsoid there are two diametral plane sections of radius  $\beta$  whose intersections with the ellipsoid are circles. Waves of light propagated along the normals to these sections behave as they would in isotropic substances. These directions are called the optic axes or optic binormals. To find the angle between the two circular sections, note that on the principal  $\alpha$ ,  $\gamma$  plane of the ellipsoid their traces are the straight lines of radius  $\beta$ . The general equation of the index ellipsoid referred to rectangular axes reads:

$$\frac{x^2}{\alpha^2} + \frac{y^2}{\beta^2} + \frac{z^2}{\gamma^2} = 1.$$

For the  $\alpha\gamma$  principal section of the ellipsoid,  $y=0$  and the equation becomes

$$\frac{x^2}{\alpha^2} + \frac{z^2}{\gamma^2} = 1. \quad (1)$$

This equation defines all points of the ellipse on the  $\alpha\gamma$  plane of the ellipsoid. For the points at the outer ends of the radius  $\beta$  we have

$$x^2 + z^2 = \beta^2 \quad \text{or} \quad \frac{x^2}{\beta^2} + \frac{z^2}{\beta^2} = 1. \quad (2)$$

Subtract equation (2) from equation (1) and obtain

$$x^2 \left( \frac{1}{\alpha^2} - \frac{1}{\beta^2} \right) + z^2 \left( \frac{1}{\gamma^2} - \frac{1}{\beta^2} \right) = 0$$

or

$$\frac{z^2}{x^2} = \frac{\frac{1}{\alpha^2} - \frac{1}{\beta^2}}{\frac{1}{\beta^2} - \frac{1}{\gamma^2}} = \tan^2 \Omega.$$

The angle between the normals to the  $\beta$  traces on the  $\alpha\gamma$  plane is the optic axial angle  $2V_\gamma$  and is the supplement to  $\Omega$ . Therefore

$$\tan^2 V_\gamma = \frac{\frac{1}{\alpha^2} - \frac{1}{\beta^2}}{\frac{1}{\beta^2} - \frac{1}{\gamma^2}}. \quad (3)$$

This is the standard equation given in text books. Other expressions derived from equation (3) are:

$$\sin^2 V_\gamma = \frac{\frac{1}{\alpha^2} - \frac{1}{\beta^2}}{\frac{1}{\alpha^2} - \frac{1}{\gamma^2}} \quad \text{and} \quad \cos^2 V_\gamma = \frac{\frac{1}{\beta^2} - \frac{1}{\gamma^2}}{\frac{1}{\alpha^2} - \frac{1}{\gamma^2}}. \quad (3a)$$

These three equations are not in a form adapted for computation. Each one expresses an equality between the square of a trigonometric function of half the desired angle and the ratio between differences of the reciprocal squares of the principal refractive indices. A more convenient expression is:

$$\cos 2V_\gamma = \cos^2 V_\gamma - \sin^2 V_\gamma = \frac{\frac{2}{\beta^2} - \left( \frac{1}{\alpha^2} + \frac{1}{\gamma^2} \right)}{\frac{1}{\alpha^2} - \frac{1}{\gamma^2}}. \quad (4)$$

This equation can be simplified with slight loss in accuracy and still yield values of  $2V_\gamma$  accurate, in general, to one minute of arc for values of the maximum birefringence  $(\gamma - \alpha)$  up to 0.050; and to three minutes of arc for values of  $(\gamma - \alpha)$  up to 0.100; and for all values of the refractive index  $\alpha$  from 1.400 to 2.000.

Let

$$\beta - \alpha = \delta, \quad \gamma - \beta = \epsilon, \quad \text{and} \quad \gamma - \alpha = \epsilon + \delta; \quad \text{or} \quad \alpha = \beta - \delta, \quad \gamma = \beta + \epsilon.$$

On substituting in equations (3a) and (4) for  $\alpha$  and  $\gamma$  the equivalent values  $\beta - \delta$  and  $\beta + \epsilon$ , and neglecting the higher order terms,  $2\epsilon^2\delta^2$  and  $-4\beta(\epsilon - \delta)\epsilon\delta$ , which are, in general, so small that for  $(\gamma - \alpha) < 0.050$  they do not influence the result, we obtain the equations:



$$\sin^2 V_0 = \frac{\delta}{\epsilon + \delta} + \frac{3\epsilon\delta}{\gamma^2 - \alpha^2} \quad (5a)$$

$$\cos^2 V_0 = \frac{\epsilon}{\epsilon + \delta} - \frac{3\epsilon\delta}{\gamma^2 - \alpha^2} \quad (5b)$$

$$\cos 2V_0 = \frac{\epsilon - \delta}{\epsilon + \delta} - \frac{6\epsilon\delta}{\gamma^2 - \alpha^2} \quad (5c)$$

These approximate equations may be used directly if the principal refractive indices are given for a specified wave length of light. Each one consists of two parts, of which the first in (5c),  $(\epsilon - \delta)/(\epsilon + \delta)$ , expresses the ratio of the difference between the two partial principal birefringences to their sum. It should be noted that this ratio alone yields values of the optic axial angle correct, in general, to 1.5° or less, for refractive index  $\alpha$  between 1.400 and 2.000 and for values of the maximum birefringence,  $\gamma - \alpha$ , from 0 to 0.050.

The ratio  $(\epsilon - \delta)/(\epsilon + \delta)$  is simply the difference between the two partial principal birefringences expressed in terms of the maximum birefringence,  $\gamma - \alpha$ , and is clearly independent of the actual values of the principal refractive indices,  $\alpha, \beta, \gamma$ . Thus if  $\alpha_1, \beta_1, \gamma_1$  refer to one crystal and  $\alpha_2, \beta_2, \gamma_2$  to a second, then  $\epsilon_1 = \gamma_1 - \beta_1, \delta_1 = \beta_1 - \alpha_1$  and  $\epsilon_2 = \gamma_2 - \beta_2, \delta_2 = \beta_2 - \alpha_2$ . If now  $(\epsilon_1 - \delta_1)/(\epsilon_1 + \delta_1)$  and  $(\epsilon_2 - \delta_2)/(\epsilon_2 + \delta_2)$  have the same ratio value,  $(\epsilon_1 - \delta_1)/(\epsilon_1 + \delta_1) = (\epsilon_2 - \delta_2)/(\epsilon_2 + \delta_2)$ , then  $\epsilon_2/\epsilon_1 = \delta_2/\delta_1 = C$ , wherein  $C$  is a constant. For a given value of  $\cos 2V_u$ , therefore, the actual refractive indices  $\alpha, \beta, \gamma$  may vary within a wide range, but only in such manner that the proportion  $\epsilon_2/\epsilon_1 = \delta_2/\delta_1 = C$  is maintained and so that the proportionality factor  $C$  cancels out in the homogeneous expression. Similar relations obtain for the correction term,  $-6\epsilon\delta/(\epsilon + \delta)(\gamma + \alpha)$ , and for equations (3a) and (4).

If a table of the angle values of  $\cos 2V_u$  extending over the range 0 to 1.0 in steps of 0.01 be prepared, the angle corresponding to a given ratio value of  $\cos 2V_u = (\epsilon - \delta)/(\epsilon + \delta)$  can be read off directly. The angle  $2V_u$  refers to that obtained from the first term of equation (5c) alone and without the second term. In table 1, these values are listed in degrees and thousandths of a degree rather than in degrees and minutes of arc. The differences between the angular values for successive steps of 0.01 are also included, so that the actual values of  $2V_u$  can be obtained by linear interpolation. For example, let  $(\epsilon - \delta)/(\epsilon + \delta) = 0.5463$ . In table 1 we find  $2V_u = 57^\circ.316$  for the ratio 0.54; and  $2V_u = 56^\circ.633$  for the ratio 0.55; the difference between these angles is  $0^\circ.683$ . Therefore the desired value for  $(\epsilon - \delta)/(\epsilon + \delta) = 0.5463$  is  $57^\circ.316$  minus  $0^\circ.683 \times 0.63 = 0^\circ.430$  or  $56^\circ.886$ . Since  $1^\circ = 60'$ , the value in minutes of  $0^\circ.886$  is  $60 \times 0.886 = 53'$  and  $56^\circ.886 = 56^\circ 53'$ . Approximate values of  $2V_u$  may be read off directly

from figure 1 which is a nomograph of the equation  $\cos 2V_u = (\epsilon - \delta) / (\epsilon + \delta)$ . The scales for the variables,  $(\epsilon + \delta)$ ,  $(\epsilon - \delta)$ , and  $\cos 2V_u$  are given on the diagram. For example, let  $\epsilon + \delta = 0.033$ ;  $\epsilon - \delta = 0.013$ . To find  $2V_u$  pass a straight line through the two points and find at its intersection with the  $2V_u$  scale,  $2V_u = 67^\circ$ . It should be noted that in this nomogram the  $\cos 2V$  scale is widely spaced for values near  $90^\circ$ , but very closely spaced near  $0^\circ$ . In other words, the scale is not uniform and more accurate results are obtainable directly from table 1, or from a large scale plot based on this table. This effect of change of scale in

TABLE 1. VALUES OF THE ANGLE  $2V_u$  FOR A SERIES OF VALUES OF  $\cos 2V_u = (\epsilon - \delta) / (\epsilon + \delta)$  RANGING IN STEPS OF 0.01 FROM 0 TO 1.0

$\frac{\epsilon - \delta}{\epsilon + \delta}$	$2 V_u$	Diff.	$\frac{\epsilon - \delta}{\epsilon + \delta}$	$2 V_u$	Diff.	$\frac{\epsilon - \delta}{\epsilon + \delta}$	$2 V_u$	Diff.	$\frac{\epsilon - \delta}{\epsilon + \delta}$	$2 V_u$	Diff.
.00	90°000		.25	75°522		.50	60°000		.75	41°410	
.01	89°427	.573	.26	74°930	.592	.51	59°336	.664	.76	40°536	.874
.02	88°854	.573	.27	74°336	.594	.52	58°668	.668	.77	39°646	.890
.03	88°281	.573	.28	73°740	.596	.53	57°995	.673	.78	38°739	.907
.04	87°708	.573	.29	73°142	.598	.54	57°316	.679	.79	37°814	.925
.05	87°134	.574	.30	72°542	.600	.55	56°633	.683	.80	36°870	.944
		.574			.601			.689			.966
.06	86°560	.574	.31	71°941	.604	.56	55°944	.694	.81	35°904	.989
.07	85°986	.575	.32	71°337	.606	.57	55°250	.701	.82	34°915	1.014
.08	85°411	.575	.33	70°731	.608	.58	54°549	.706	.83	33°901	1.041
.09	84°836	.575	.34	70°123	.610	.59	53°843	.713	.84	32°860	1.072
.10	84°261	.576	.35	69°513	.613	.60	53°130	.720	.85	31°788	1.105
		.576			.616			.726			1.142
.11	83°685	.577	.36	68°900	.618	.61	52°410	.734	.86	30°683	1.183
.12	83°108	.578	.37	68°280	.620	.62	51°684	.742	.87	29°541	1.231
.13	82°530	.578	.38	67°666	.624	.63	50°950	.750	.88	28°358	1.285
.14	81°952	.579	.39	67°046	.627	.64	50°208	.758	.89	27°127	1.347
.15	81°373	.580	.40	66°422	.630	.65	49°458	.767	.90	25°842	1.421
		.580			.633			.777			1.509
.16	80°793	.581	.41	65°795	.636	.66	48°700	.786	.91	24°495	1.617
.17	80°212	.582	.42	65°165	.640	.67	47°933	.797	.92	23°074	1.753
.18	79°630	.583	.43	64°532	.643	.68	47°156	.808	.93	21°565	1.935
.19	79°047	.584	.44	63°896	.647	.69	46°370	.819	.94	19°948	2.190
.20	78°463	.585	.45	63°256	.651	.70	45°573	.832	.95	18°195	2.592
		.585			.656			.845			3.368
.21	77°878	.587	.46	62°613	.659	.71	44°765	.859	.96	16°260	8.110
.22	77°291	.588	.47	61°966		.72	43°946		.97	14°070	
.23	76°703	.590	.48	61°315		.73	43°114		.98	11°478	
.24	76°113	.591	.49	60°659		.74	42°269		.99	8°110	
.25	75°522		.50	60°000		.75	41°410		1.00	0°000	

different parts of a nomogram is common to many nomographs and should be recognized by the user.

In case the refractive indices  $\alpha$ ,  $\gamma$  are given, and only  $\beta$  is allowed to vary, the maximum birefringence,  $\gamma - \alpha$ , remains constant, while the partial principal birefringences,  $\epsilon = \gamma - \beta$  and  $\delta = \beta - \alpha$ , vary in opposite directions, such that when  $\epsilon = 0$ ,  $\gamma = \beta$ , the crystal is uniaxial and

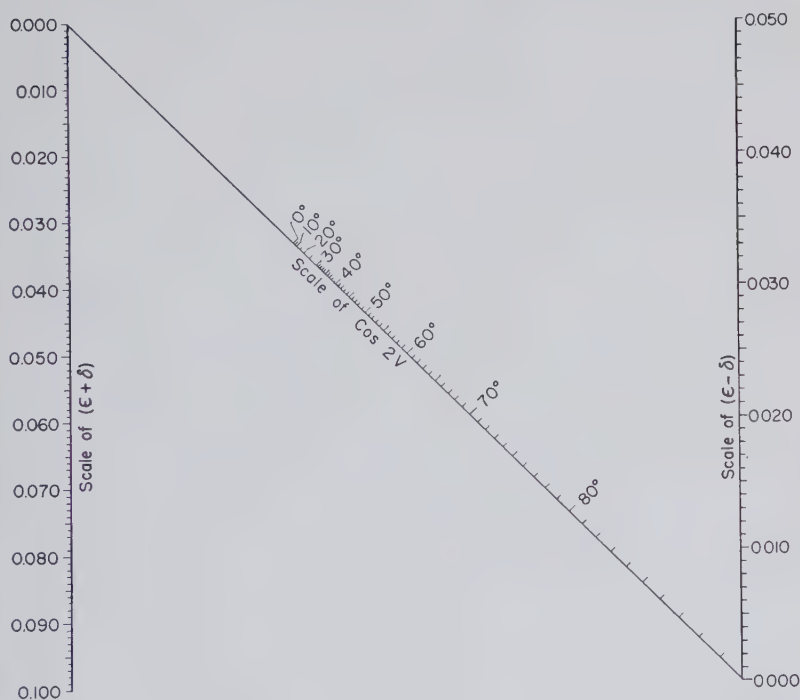


FIG. 1. Nomogram solution of the equation  $\cos 2V = (\epsilon - \delta) / (\epsilon + \delta)$ . The scale for  $(\epsilon - \delta)$  is the ordinate on the right side of the diagram; that for  $(\epsilon + \delta)$ , on the left side, while that for  $\cos 2V$  is on the diagonal line of the diagram.

optically negative with  $\alpha$  the optical axis; when  $\delta = 0$ ,  $\beta = \alpha$ , the crystal is uniaxial and optically positive with  $\gamma$  the optical axis. In all other cases the crystal is biaxial. When  $\epsilon = \delta$ ,  $\epsilon - \delta = 0$ , the crystal is biaxial and  $\cos 2V_u = 0$  or  $2V_u = 90^\circ$ .

The second term of equation (5c),  $-6\epsilon\delta/(\alpha + \gamma)(\epsilon + \delta)$ , is of the nature of a correction term (C.T.) by means of which the value of  $2V_e$  can in general be determined to  $1'$  of arc when  $(\gamma - \alpha)$  does not exceed 0.050. In case the value of  $\cos 2V_e$  is extremely small (0.05 to 0), the error may be greater, because the angle  $2V_e$  changes rapidly for slight changes in the value of  $\cos 2V_e$  as it approaches zero and linear interpolation in



that region is inexact. The correction term itself consists of a constant,  $6/(\alpha + \gamma)$ , multiplied by the ratio  $\epsilon\delta/(\epsilon + \delta)$  in which the numerator is the product  $\epsilon\delta$  and the denominator, the sum  $(\epsilon + \delta)$ . It was proved in a preceding paragraph that for a definite value of  $(\epsilon - \delta)/(\epsilon + \delta)$  various partial principal birefringences are possible; but that, to maintain the ratio constant, both  $\epsilon$  and  $\delta$  must increase or decrease in the same proportion; and also that  $(\epsilon_2 + \delta_2) = C(\epsilon_1 + \delta_1)$ . Therefore,  $\epsilon_2\delta_2/(\epsilon_2 + \delta_2) = C^2\epsilon_1\delta_1/C(\epsilon_1 + \delta_1) = C\epsilon_1\delta_1/(\epsilon_1 + \delta_1)$ ; in other words, the value of the ratio is proportional to the increase of  $(\epsilon_2 + \delta_2)$  over  $(\epsilon_1 + \delta_1)$ . It follows that if, for a given value of  $(\epsilon_1 - \delta_1)/(\epsilon_1 + \delta_1)$ , we plot the change in the value of the fraction  $\epsilon_2\delta_2/(\epsilon_2 + \delta_2)$  against the change in the maximum principal birefringence,  $\epsilon_2 + \delta_2 = \gamma_2 - \alpha_2$ , the result will be a straight line passing through the point,  $\epsilon_1\delta_1/(\epsilon_1 + \delta_1)$ . It is possible, therefore, to compute the values of the correction term for one maximum principal birefringence, such as  $\gamma_1 - \alpha_1 = \epsilon_1 + \delta_1 = 0.010$  and from them to obtain the values for any other maximum birefringence and for a given refractive index  $\alpha_2$  by multiplication by the factor  $(\gamma_2 - \alpha_2)/0.010 = C$ .

In table 2, the results of the computation are listed for each change of 0.1 in the ratio  $(\epsilon - \delta)/(\epsilon + \delta)$ ; in this table the values listed are given directly in terms of the angle value of  $2V_u$  corresponding to the change in the decimal value of  $\cos 2V_u$ . This is permissible because, for the small changes under consideration, the rates of change in the decimal values of  $\cos 2V_u$  are, as a rule, proportional to the changes in the values of  $2V_u$  itself.

To compute the value of the correction term for a given refractive index  $\alpha'$ , and for a given birefringence,  $(\gamma' - \alpha')$ , when the value of the term is known for another refractive index,  $\alpha$ , and for the same birefringence,  $(\gamma - \alpha)$ , multiply the known value by the factor of proportionality  $1/C = \alpha/\alpha'$ . For example, let  $\alpha = 1.400$ ,  $\gamma = 1.410$ , and  $\gamma - \alpha = 0.010$ ; for  $(\epsilon - \delta)/(\epsilon + \delta) = 0.80$ , the value of the correction term is found to be  $0.0019217 = 0^\circ.300$ . For the refractive index,  $\alpha' = 2.000$ , we have  $\alpha/\alpha' = 1.400/2.000 = 0.7$ , and find for the correction term the value,  $0.7 \times 0.0019217 = 0.0013452 = 0^\circ.210$ . The computed value is that of the exact equation (4) minus the value of the first part of equation (5c) and is  $0^\circ.212$ .

In principle this method is similar to that advocated by E. S. Larsen, Jr. (1921) who prepared a correction chart based on the refractive index 1.500 to serve in finding the correction to be applied to the value of  $2V_\gamma$  or  $2V_\alpha$  obtained by use of the approximate formula of Mallard (1884, p. 413).

By use of tables 1 and 2, it is thus possible to read off directly the approximate value of  $2V_c$  (subscript *c* signifies 'computed') for any values



of the principal refractive indices which are likely to occur. Experience has shown that in certain cases time is saved by disregarding the tables and by using equation (5c) directly, either together with a table of logarithms or with a calculating machine and a table of natural trigonometric functions.

In connection with the usefulness of the above method, the relative frequency of the occurrence of maximum principal birefringences,  $\gamma - \alpha$ , in various minerals and in crystals prepared in the laboratory is important. Thus, of 887 biaxial minerals listed by Larsen and Berman (1934) and of 154 inorganic crystallized salts listed by Fry (1922) the total number for which  $(\gamma - \alpha)$  is between 0.001 and 0.010 is 178; between 0.011 and 0.020 it is 245, and so on.

In table 3 the distribution is shown of the numbers of minerals and of inorganic salts which have a given range in principal birefringence,  $\gamma - \alpha$ ; under each heading the percentage distribution is listed also. The last two columns give the total number, minerals plus inorganic salts, and the cumulative percentages. The table shows that more than three fourths of the biaxial crystals (positive and negative) have a maximum birefringence,  $\gamma - \alpha$ , between 0.001 and 0.050. For roughly 14 per cent of the crystals, the birefringence,  $\gamma - \alpha$ , is between 0.051 and 0.100; while, for values of  $(\gamma - \alpha)$  exceeding 0.100, the percentage is about 11. It follows, therefore, that the use of equations 5a, 5b, 5c is justified in about three-fourths of biaxial minerals and inorganic crystals whose birefringence,  $\gamma - \alpha$ , ranges between 0.001 and 0.050. The accuracy in the value of  $2V$  is then about  $1'$  of arc; and for roughly nine-tenths of biaxial crystals for which  $(\gamma - \alpha)$  is between 0.001 and 0.100, it may reach  $3'$  or  $4'$  of arc.

Equation (5c) shows that in case  $\epsilon = \delta$  or  $(\epsilon - \delta)/(\epsilon + \delta) = 0$ ,  $\cos 2V_u = 0$  and  $2V_u = 90^\circ$ , but the second term (C.T.) is negative and hence  $2V_e$  is greater than  $90^\circ$ ;  $\alpha$  is then the acute bisectrix and the crystal is optically negative. In general, biaxial crystals for which the partial birefringence,  $\beta - \alpha$ , is greater than the partial birefringence,  $\gamma - \beta$ , or  $\delta > \epsilon$ , are optically negative and  $\alpha$  is the acute bisectrix. Biaxial crystals for which  $(\gamma - \beta)$  is greater than  $(\beta - \alpha)$ , or  $\epsilon > \delta$ , are, as a rule, optically positive with  $\gamma$  the acute bisectrix.

In this connection it is of interest to ascertain how much the midway value of  $\beta = (\alpha + \gamma)/2$  may depart from equality to convert the crystal from one of optically negative character to one of positive character. To find the refractive index  $\beta$  for which  $\cos 2V = 0$  when  $\alpha$  and  $\gamma$  are given, we observe from equation (4) that then

$$\frac{2}{\beta^2} = \frac{1}{\alpha^2} + \frac{1}{\gamma^2}. \quad (6)$$



TABLE 3. RELATIVE FREQUENCY OF BIAxIAL CRYSTALS (MINERALS AND INORGANIC SALTS) FOR VARIOUS PRINCIPAL BIREFRINGENCES ( $\gamma-\alpha$ ) IN INTERVALS OF 0.010 FROM 0 TO 0.100, AND FOR LARGER INTERVALS IN CRYSTALS OF STRONGER BIREFRINGENCE.

IN THE LAST TWO COLUMNS OF THIS TABLE THE RELATIVE FREQUENCY IN THE SAME SET OF MINERALS IS LISTED WITH REFERENCE TO THE LEAST PRINCIPAL REFRACTIVE INDEX  $\alpha$

$\gamma-\alpha$	Minerals		Inorganic Salts		Total		$\alpha$	Minerals	
	No.	Per Cent	No.	Per Cent	No.	Per Cent	1. 1.	No.	Cumulative Per Cent
0.001-.010	146	16.5	32	20.8	178	17.1	300-399	7	0.1
.011-.020	201	22.7	44	28.6	245	40.6	400-499	100	11.8
.021-.030	167	18.8	25	16.2	192	59.1	500-599	236	37.9
.031-.040	89	10.0	7	4.5	96	68.3	600-699	281	69.0
.041-.050	63	7.1	12	7.8	75	75.5	700-799	153	86.0
	666	75.1	120	77.9	786			777	
.051-.060	37	4.2	4	2.6	41	79.4	800-899	37	90.0
.061-.070	29	3.3	1	0.6	30	82.3	900-999	20	92.3
.071-.080	26	2.9	5	3.2	31	85.3	2. 2.		
.081-.090	24	2.7	3	1.9	27	87.9	000-099	16	94.0
.091-.100	14	1.6	3	1.9	17	89.5	100-199	19	96.1
	130	14.7	16	10.2	146			92	
.101-.150	47	5.3	8	5.2	55	94.8	200-299	12	97.5
.151-.200	21	2.4	4	2.6	25	97.2	300-399	10	98.6
.201-.250	9	1.0	3	1.9	12	98.4	400-499	5	99.1
.251-.300	4	0.5	1	0.6	5	98.8	500-749	4	99.6
.301-.400	7	0.8	2	1.3	9	99.7	750-999	1	99.7
.401-.500	1	0.1	0	0.0	1	99.8	3. 3.		
.501-.600	1	0.1	0	0.0	1	99.9	000-999	3	100.0
.601-1.20	1	0.1	0	0.0	1	100.0			
	91	10.3	18	11.6	109			35	
Total	887	100.1	154	99.7	1041			904	

For  $\alpha=1.500$  and for  $\gamma-\alpha=0.010, 0.020, 0.030, 0.040, 0.050$ , and  $0.100$  respectively, we find from equation (6) the values to be:  $\beta=1.504975, 1.509901, 1.514777, 1.519605, 1.524385$ , and  $1.547582$ . In these cases the differences between the values listed and the midway values of  $\beta$  are, respectively:  $0.000025, (0.08'), 0.000099 (0.30')$ ,

0.000223 (0.78') 0.000395 (1.36') 0.000615 (2.11'), 0.002418 (8.32'). For  $\alpha=2.000$ , the corresponding differences are, respectively: 0.000019 (0.07'), 0.000075 (0.26'), 0.000167 (0.58'), 0.000297 (1.02'), 0.000463 (1.59'), 0.001829 (6.29'). These figures prove that with increase in  $(\gamma-\alpha)$ , the departure of  $2V$  from  $90^\circ$  increases appreciably, but that the total departure does not exceed  $10'$  of arc. If  $\gamma-\alpha=0.100$ , the actual change in  $\beta$  may exceed 0.002, a quantity which is easily measurable and which might cause trouble were the above rule on the optical character of a biaxial crystal followed literally. However, the chance of error from this source is slight and is likely to occur only in biaxial crystals of strong birefringence.

The data of tables 1 and 2 together with the linear relations between the birefringence,  $\gamma-\alpha$ , and the second term of equation (5c) can be represented by three simple charts. Experience has proved, however, that the degree of accuracy obtainable by their use is appreciably less than that from equation (5c) or from the tables. In many cases the accuracy attainable from the first term alone of equation (5c) is quite adequate, especially in crystals of low birefringence and for which the principal refractive indices are given only to the third decimal place. In these cases a shift of only one unit in the third decimal place may produce a change in the value of the optic axial angle of  $10^\circ$  or  $20^\circ$  or even  $30^\circ$ . For this reason it is not surprising in tables of the optical properties of biaxial crystals to note a wide discrepancy between the measured optic axial angle,  $2V$ , listed and that computed from either the exact equation (3) or (4) or from the approximate equation (5) given above. In general and for many purposes, the value  $2V_u$  computed from the first term of equation (5c) suffices. This term alone shows that the value of the optic axial angle depends chiefly on the difference of the two partial principal birefringences,  $(\gamma-\beta)-(\beta-\alpha)$ , divided by the maximum principal birefringence  $(\gamma-\alpha)$ . As a result, the value of  $2V$  is extremely sensitive to slight changes in the values of the principal refractive indices, especially of  $\beta$ . It is, therefore, not advisable to use the optic axial angle in conjunction with any two principal refractive indices to find the third refractive index. If  $\alpha$ ,  $\gamma$ , and  $2V$  are given, the chances of ascertaining  $\beta$  with fair accuracy are better than when  $\alpha$ ,  $\beta$ ,  $2V$ , or  $\beta$ ,  $\gamma$ ,  $2V$  are given to find  $\gamma$  or  $\alpha$ , respectively.

*Historical.* Several investigators have sought to simplify the computations involved in equations (3) and (3a). Mallard (1884) proposed that in equations (3) and (3a) the principal birefringences,  $\gamma-\alpha$ ,  $\gamma-\beta$ ,  $\beta-\alpha$ , be substituted for the differences between the reciprocal squares of the corresponding principal refractive indices. He noted that for biaxial crystals of medium to weak birefringence the approximation is in general

sufficiently close to the exact value to be satisfactory. In line with Mallard's suggestion the expression in equation (4) may be changed to read:  $\cos 2V_\gamma = \cos^2 V_\gamma - \sin^2 V_\gamma = (\gamma - \beta)/(\gamma - \alpha) - (\beta - \alpha)/(\gamma - \alpha) = (\gamma + \alpha - 2\beta)/(\gamma - \alpha)$ . Computations show that this equation for  $2V_u$  yields values for  $2V$  correct to 1°5 for crystals whose birefringence,  $\gamma - \alpha$ , does not exceed 0.050. With increase in birefringence,  $\gamma - \alpha$ , the degree of accuracy decreases appreciably; thus for  $\alpha = 1.500$  and  $\gamma - \alpha = 0.100$  the error is 2°773; for  $\alpha = 2.000$  and  $\gamma - \alpha = 0.100$ , it is 2°096.

In 1911 (Plate 9) Wright published a graphical chart based on the equation  $\sin^2 V_\gamma = (\beta - \alpha)/(\gamma - \alpha)$  from which, having given  $\beta - \alpha$  and  $\gamma - \alpha$ , the value of  $V_u$  can be read off directly. The chart extends to values of  $\gamma - \alpha = 0.090$  and  $\gamma' - \alpha' = 0.090$ . It would have been better had the chart been extended to  $\gamma - \alpha = 0.100$  and  $\gamma' - \alpha' = 0.100$ , and in the labeling of the optic axial angle, had  $2V_u$  been used for  $V_u$ .

In 1912 Boldyrew published three diagrams based on the exact equation  $\tan V_\gamma = \gamma\sqrt{\beta^2 - \alpha^2}/\alpha\sqrt{\gamma^2 - \beta^2} = (\beta + \epsilon)\sqrt{\beta^2 - (\beta - \delta)^2}/(\beta - \delta)\sqrt{(\beta + \epsilon)^2 - \beta^2}$ . When  $\beta$  is known, this equation defines relations between the partial birefringences  $\epsilon = \gamma - \beta$ ,  $\delta = \beta - \alpha$ , and  $V_\gamma$ . If  $V_\gamma$  be known, then for any value of  $\epsilon$  a corresponding value of  $\delta$  is given. Let the values of  $\epsilon$  be the abscissae and those of  $\delta$  the ordinates. A series of curves for  $V_\gamma$  is thus obtained by computation which enables the observer to read off directly the value of the third variable when the other two are known. For each diagram one  $\beta$  is valid, namely,  $\beta = 1.500$ ,  $\beta = 1.650$ , and  $\beta = 2.000$ . These charts are interesting, but they have not come into general use.

In 1913 (Plates VI and VII) F. E. Wright published two charts for the solution of the equation (3), (Plates VI and VII); with these a table of the values of reciprocal squares of refractive indices was included. In Plate VI the values of  $1/\alpha^2 - 1/\beta^2$  are abscissae, those of  $1/\beta^2 - 1/\gamma^2$ , the ordinates, and the series of straight lines radiating from zero, the values of  $V_\alpha$ . In Plate VII the values of  $(1/\alpha^2 - 1/\beta^2)^{1/2}$  are the abscissae, those of  $(1/\beta^2 - 1/\gamma^2)^{1/2}$  the ordinates, while the radiating straight lines denote the values of  $V_\alpha$ . In Plate VII the distribution of the  $V_\alpha$  values is more uniformly spread and for this reason is superior to Plate VI. It should be noted that both Plates serve equally well for the approximate equations  $\tan^2 V_\alpha = (\gamma - \beta)/(\beta - \alpha)$  and  $\tan V_\alpha = [(\gamma - \beta)/(\beta - \alpha)]^{1/2}$ .

In 1927 Roesch and Sturenborg suggested a modification of the exact equation (3) and expressed it in the form  $\tan^2 V_\gamma = (\gamma/\alpha)^2(\beta/\alpha)^2 - 1)/(\gamma^2/\alpha^2 - \beta^2/\alpha^2)$  in which the ratios,  $\beta/\alpha$  and  $\gamma/\alpha$ , are given. In order that this form be useful, the writers computed a series of tables for the two ratios and presented the solutions of the equation in two graphs of curves

from which the value of the optic axial angle can be read off directly. This method, though interesting, has not been used greatly.

In 1937 Smith, on the basis of Plate VI of the above paper by F. E. Wright and for the approximate equation,  $\tan^2 V_\gamma = (\beta - \alpha) / (\gamma - \beta)$ , published a new diagram by which, with the aid of a sliding scale, he was able to read off directly and without computation the values of the partial birefringences or of their ratio. In his chart a central vertical line divides it into a positive and a negative section. On the sliding scale, which is divided uniformly into convenient units, the value of  $\alpha$  on the scale is placed on the left of the central line; the scale division for  $\beta$  is placed at the central mark on the base line of the diagram, and that of  $\gamma$  on the right of  $\beta$ . The intersection of the N.E. diagonal line through  $\alpha$  on the scale with the N.W. diagonal through  $\gamma$  determines the position of the straight line  $\beta$  and thereby the angle  $V_\gamma$  (labeled  $2V_\gamma$  for convenience), and also the optical character of the crystal, whether positive or negative. Smith's chart is convenient, but, as Smith emphasizes, its accuracy is not high for weak birefringences because of the clustering of the lines near their point of intersection.

In 1938 Lane and Smith described another chart for the solution of the approximate equation. This chart requires the use of a sliding scale but of a different kind. The chart is said to be more satisfactory for crystals of low birefringence than is the Smith chart. However, neither chart has been used widely.

In 1942 Mertie described a nomographic chart based on the exact sine equation (3a). The Mertie chart is self-contained in the sense that if the three principal refractive indices are known, the optic axial angle and the optical character can be read off directly by use of a straight edge or of a straight line and without computation of any kind. In the nomograph the horizontal scale, which determines the spacing of the vertical lines, is  $\sin^2 V_\gamma$ ; the vertical scale, which determines the spacing of the horizontal lines, is  $1/n^2$ . On the left side of the plot the scale is  $1/\alpha^2$  or  $1/\beta^2$ , but it is marked  $\alpha$  or  $\beta$ ; on the right side the scale is the same as that on the left (function  $\sin^2 V_\gamma$ ), but it refers to  $1/\gamma^2$  or  $1/\beta^2$  and is labeled  $\gamma$  or  $\beta$ . Similarly  $V_\gamma$  extends on the left side of the diagram from  $0^\circ$  to  $45^\circ$  and is marked positive; on the right side of the diagram,  $V_\alpha$  extends in the reverse direction from  $0^\circ$  to  $45^\circ$  and is marked negative. Since the user of the diagram is interested chiefly in  $2V_\gamma$  and  $2V_\alpha$ , it might have been wise to label on the positive side the angles  $2V_\gamma$  as from  $0^\circ$  to  $90^\circ$ , and similarly on the negative side.

In a second nomograph Mertie solves directly the equation  $\sin^2 E / \beta^2 = (1/\alpha^2 - 1/\beta^2) / (1/\alpha^2 - 1/\gamma^2)$ , thus avoiding the need for a second nomograph for the equation  $\sin E = \beta \sin V$ .



It is obvious that because of the closer spacing of the horizontal lines with increase in value of  $\alpha$  and because the scale for  $\sin^2 V_\gamma$  is more closely crowded for small values of  $V_\gamma$ , the degree of accuracy of the plot varies appreciably in its several sections. For minerals of low birefringence, say  $\gamma - \alpha = 0.010$ , the error in determination of  $2V_\gamma$  may be several degrees because of the acute angle between a horizontal line and the straight line passed through  $\alpha$  on the left side and through  $\gamma$  on the right side of the diagram. Under these conditions a very small error in the spacing of the horizontal lines on the chart produces a significant error in the optic axial angle. As the result of a number of test readings on the chart and a comparison with the values obtained by direct computation by the exact formula, it may be stated that the error made by use of the Mertie chart is in general somewhat less than that obtained by use of the simple chart of figure 1, based on the approximate Mallard equation. The average error of the readings of  $2V$  from the Mertie chart for various refractive indices and various birefringences was one degree. Many of the readings were too high; some were too low, as might be expected.

In 1945 Waldmann published a nomogram based on equation (3). By reducing the index ellipsoid to one in which the  $\beta$ -axis is unity and adopting the ratios,  $A = \alpha/\beta$  and  $C = \gamma/\beta$ , whereby  $\alpha$  and  $\gamma$  are expressed in terms of  $\beta$ , he obtains from equation (3) the form  $\tan^2 V = (1/A^2 - 1)/(1 - 1/C^2)$ , in which two independent variables instead of three occur. To find the values of  $1/A^2$  and  $1/C^2$  he plots the values of  $\beta^2$  along the ordinate axis and  $1/A^2$  and  $1/C^2$  along the abscissa, with the origin of coordinates on the right. Through the ordinate,  $n^2 = 0$  at abscissa  $x = 0$ , radiating lines are drawn across the diagram. The intersections of these lines with the horizontal line through the ordinate at  $\beta^2$  yield the values of  $(1/A^2 - 1)$  on the left of ordinate at  $x = 1$  and of  $(1 - 1/C^2)$  on the right. These values are labeled  $A$  and  $C$ ; for convenience, the scale of the  $x$ -axis is made 4-times that of the  $y$ -axis. To find the optic axial angle a second diagram is used which consists of a right angle triangle whose sides include an angle of  $+45^\circ$  and  $-45^\circ$  respectively with the ordinate at  $x = 1$ . The sides of the triangle are graduated in units of the abscissae of the first diagram increased in the amount,  $1/\cos 45^\circ$ .

Theoretically the nomogram is correct and interesting; but for small values of  $V$  it is unsatisfactory in practice, even when only a portion of the original diagram is used and a correspondingly larger scale is adopted, as has been done by Burri (1950, p. 49 and Plate 1). The crowding of the diagonal lines through the apex of the triangle might be avoided by use of a nomogram based on equation (4); but experience has proved that the Mertie nomogram is better suited to the purpose.

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# X-RAY EXAMINATION OF URANOTHORITE

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## ABSTRACT

Earlier x-ray studies of thorite have indicated that it is metamict (Vegard, 1916) or have led to cell dimensions (Boldyrev, 1938) that seem out of line with those of related materials.

Single crystal x-ray diffraction patterns have been obtained from unaltered uranothorite from Gillespie's Beach, South Westland, New Zealand. Rotation patterns on the  $a$  and  $c$  axes are very similar to zircon patterns but show a certain amount of streaking along "powder arcs." A cell of dimensions  $a_0$  7.12 Å,  $c_0$  6.32 Å contains 4ThSiO<sub>4</sub>. Th is substituted by U in the ratio of about 1/7. Observed and calculated densities agree at  $6.7 \pm 0.05$ . The space group is  $D_{4h}^{19} - I4/amd$ . The similarity of the rotation patterns to those of zircon leaves no doubt that the structure of this uranothorite is of the  $H3$  (zircon) type.

## MATERIAL

Through the courtesy of Professor C. O. Hutton of Stanford University the writer received some single crystals of uranothorite for x-ray study. This uranothorite consists of minute detrital grains concentrated from sand of Gillespie's Beach, South Westland, New Zealand. It has recently been described and pictured by Hutton (1950). The material available for study comprised about a score of small rough prismatic crystals, closely resembling Hutton's Fig. 47, Plate 3. The largest of these was about 0.18 by 0.10 millimeter. The total weight of the sample was less than half a milligram.

## X-RAY EXAMINATION

Rotation patterns were made from three crystals. These included  $c$  axis patterns from two crystals and an  $a$  axis pattern from another. Calibration of the films was obtained by photographing the  $c$  axis zero layer line of quartz on the same film between the zero and first layer lines of the specimen being examined.<sup>1</sup> All patterns were made with Cu radiation, filtered by Ni, in a camera of 57.3 mm. diameter.

As may be seen from Fig. 1 (top) the patterns are closely similar to those obtained from zircon. The differences are of two sorts. All spots on the uranothorite patterns are closer to the center due to the greater cell dimensions. Spots on all uranothorite patterns are streaked along "powder arcs." They are not broadened or frayed. High intensities are observed even at large angles. This suggests a disorientation of mosaic

<sup>1</sup> This is easily accomplished in a Weissenberg camera by replacing the beam catcher with the layer line screen set for the zero level, displacing the camera parallel to the rotation axis about half the distance between the zero and first layer lines of the material under study and recording a quartz  $c$  axis pattern with this screening.

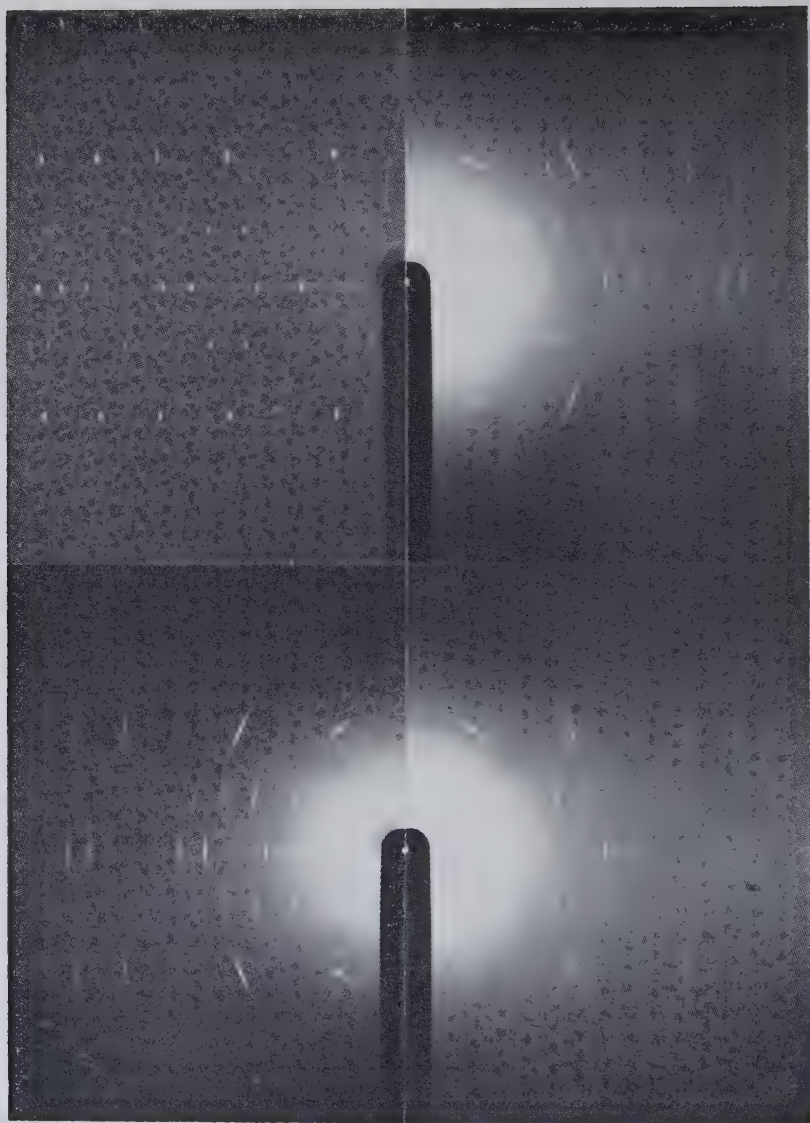


FIG. 1. *c* axis rotation patterns

*Top left*

Zircon, near Lincoln, California

Exposure 2 hours

*Bottom left*

Same crystal as used for top right after  
heating to 850° for 75 minutes,  
Exposure 20 hours

*Top right*

Uranothorite, Gillespie's Beach, S. West-  
land, N. Z.

Exposure 25 hours

*Bottom right*

Same as above.



blocks more or less uniformly distributed over a small angular range.

The cell dimensions, taking  $\text{CuK}\alpha$  as  $1.542 \text{ \AA}$ , derived from these patterns are:

$$\begin{aligned}a_0 & 7.12 \pm 0.03 \text{ \AA} \\ c_0 & 6.32 \pm 0.03 \text{ \AA}\end{aligned}$$

The space group, indicated by systematic extinctions, is  $D^{19}_{4h} - I4/amd$ , the same as for zircon. The close correspondence in the intensities of all observed diffraction spots to those of zircon leaves no doubt that the structure is of the same type,  $H3$ .

Table 1 shows the results of a calculation of the cell content. The analysis there quoted was "recalculated to 100% after eliminating

TABLE 1. CELL CONTENT OF URANOTHORITE

	A		B		C	
	Wt%	Cell Content	Wt%	Cell Content	Wt%	Cell Content
Pb	0.47	0.03				
UO <sub>2</sub>	11.5	0.55	12.3	0.59		
ThO <sub>2</sub>	62.6	3.06	67.9	3.32	81.5	4.00
CeO <sub>2</sub>	1.1	0.08	1.2	0.09		
Fe <sub>2</sub> O <sub>3</sub>	2.3	0.18				
CaO	0.3	0.07				
MgO	0.3	0.10				
SiO <sub>2</sub>	19.5	4.20	18.6	4.00	18.5	4.00
H <sub>2</sub> O—	0.25	1.38				
H <sub>2</sub> O+	1.68					
	100.00					
G <sub>obs.</sub> 6.7 ± 0.05 Uranothorite, Gillespie's Beach, South Westland, N.Z. Analyst F. T. Seelye, Hutton (1950)			G <sub>calc.</sub> 6.70 4(Th, U, Ce)SiO <sub>4</sub>		G <sub>calc.</sub> 6.72 4ThSiO <sub>4</sub>	

zircon, scheelite, ilmenite and 1.83% of undetermined material." The density given with the analysis and used in the cell content calculation is not that previously published with the analysis (Hutton 1950, Table 11, column A). It is a value determined by micropycnometer "using approximately 8 mgm. portions of pure uranothorite" (Hutton 1950, p. 678) and stated by Hutton (private communication, August 12, 1950) to be preferable to the lower figure previously published with this analy-

sis which was determined on the analyzed material including the impurities mentioned above.

The cell content obtained from the analysis suggests that this uranorthorite, aside from being contaminated, has an excess of  $\text{SiO}_2$  or a deficiency of  $\text{ThO}_2$  and substituents. A similar departure from the ideal proportions has been found in many other thorites, which, however, are metamict and contain much more water. The observed density agrees within the limits of error with the density calculated for an ideal uranorthorite of the observed cell dimensions with the proportions of Th/U/Ce indicated by the analysis (Table 1, column *B*) or with the ideal composition  $\text{ThSiO}_4$  (Table 1, column *C*).

#### COMPARISON WITH PREVIOUS WORK

The isomorphism of thorite with zircon has long been recognized but crystals of thorite suitable for precise goniometric measurement have not been found. The axial ratio usually quoted for thorite,  $a:c=1:0.6402$ , nearly the same as for zircon,  $a:c=1:0.6404$ , is based on "measurement of two crystals of orangeite" "made with a common goniometer" by E. Zschau, and reported by him in a letter to G. J. Brush.<sup>2</sup> Measurements were given to  $\frac{1}{4}^\circ$ . The axial ratio corresponding to the cell dimensions here reported is  $a_0:c_0=1:0.888=1:0.628\sqrt{2}$ , the structural cell being turned  $45^\circ$  from the usual morphological setting. This corresponds to a difference from the angles measured by Zschau of about  $\frac{1}{2}^\circ$ . One of the crystals examined gave measurable reflections from prism and pyramid faces but due to the small size and roughness of the crystal an uncertainty of at least  $\frac{1}{2}^\circ$  attached to the measurement.

X-ray observations on thorite have previously been reported by Vegard (1916) and by Boldyrev (1938). Vegard obtained only very weak and diffuse diffraction effects as was to be expected from the metamict material he examined. He reported no cell dimensions.

Boldyrev published a powder pattern of thorite from "Lövö, Langesundfjord in Norway" with the comment "This pattern has only the lines with rather weak intensity as consequence of transformation of nearly whole mass of mineral to metamict state i.e. isotropic state of secondary origin." Nevertheless he indexed the pattern and derived the cell dimensions  $a_0$  6.315,  $c_0$  5.667. The writer has previously pointed out (Pabst and Hutton, 1950) that these dimensions "are to be regarded with some reserve" because such a cell would have a much smaller volume than might be expected from a knowledge of the cell volumes of zircon and of the newly recognized monoclinic thorium silicate, huttonite (Pabst and Hutton, 1950). No powder pattern was prepared from the

<sup>2</sup> Sixth supplement to Dana's Mineralogy, *Am. J. Sci.*, **26**, 359 (1858).

TABLE 2. POWDER PATTERNS OF NATURAL THORIUM SILICATES

Uranothorite, New Zealand (calculated)			Thorite, Norway (quoted from Boldyrev, 1938)			Huttonite, New Zealand (amplified from Pabst and Hutton, 1950)		
<i>I</i>	<i>d</i> <sub>calc.</sub>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i> <sub>obs.</sub>	<i>hkl</i>
st.	4.73	011				3	5.29	$\bar{1}01$
						5	4.71	011
						6	4.23	$\bar{1}11$
v.st.	3.56	200				4	4.08	101
						4	3.53	111
						6	3.29	200
			1	3.141	200	8	3.09	120
m.-st.	2.84	121				3	2.98	210
st.	2.68	112	3	2.855	120, 002	7	2.89	$\bar{1}12, 012$
			4	2.583	102	3	2.65	202
m.-st.	2.52	220						
						3	2.48	$\bar{2}12$
						1	2.44	112
st.	2.22	031	1	2.233	220	4	2.19	031
						2	2.156	$\bar{1}03, \bar{3}11$
						3	2.110	221
w.	2.020	013						
			1	1.984	301, 130	4	1.953	212
m.	1.874	321	2	1.882	003, 311	3	b 1.893	
						2	1.857	
v.st.	1.834	312						
						2	1.810	
st.	1.780	040				2	1.784	
m.	1.757	123						
						4	b 1.749	
						2	1.692	
m.	1.667	411	3	1.665	321			
						2	1.646	
						3	1.603	
m.-st.	1.592	420						
w.	1.580	004	2	1.579	400			
w.	1.576	033						
						3	b 1.550	
w.-m.	1.482	332				1	1.486	
						2	b 1.454	
w.-m.	1.444	024						
w.	1.440	323						
			1	1.418	420			

uranothorite examined but one can calculate what it would be like with great assurance. This has been done. Table 2 shows the results of this calculation for spacings down to 1.40. It will be noted that there is little correspondence with Boldyrev's pattern. Likewise, his pattern shows no agreement with the observed pattern of huttonite. It may further be noted that the indices 120, 102, 130, 003 and 311 given by Boldyrev would be incompatible with the zircon-thorite space group. No reconciliation of these discrepancies has been found.

TABLE 3. PHYSICAL CONSTANTS OF NATURAL THORIUM SILICATES

	<i>Uranothorite</i>		<i>Huttonite</i>	
Space Group	<i>I</i> 4/ <i>amd</i>		<i>P</i> 2 <sub>1</sub> / <i>n</i>	
Cell dimensions	<i>a</i> <sub>0</sub>	7.12 Å	<i>a</i> <sub>0</sub>	6.80 Å
			<i>b</i> <sub>0</sub>	6.96
	<i>c</i> <sub>0</sub>	6.32	<i>c</i> <sub>0</sub>	5.54
Cell volume	320	Å <sup>3</sup>	299	Å <sup>3</sup>
Density (Obs.)*	6.7		7.1	
Refractive Indices*	$\alpha$	1.818–1.825	$\alpha$	1.898
	$\gamma$	1.839–1.840	$\beta$	1.900
			$\gamma$	1.922

\* As determined by C. O. Hutton.

In view of the possibility that heat treatment might effect a transformation between the two natural thorium silicates whose constants are contrasted in Table 3, a crystal of uranothorite which had been used for a *c*-axis rotation pattern was dismantled and subjected to a temperature of 850° C. in a platinum crucible in a furnace for 75 minutes. The crystal suffered no visible change. As may be seen from Fig. 1 (bottom) no substantial changes are indicated by comparison of the patterns. If anything, the pattern of the heated material is slightly sharper. Though it is evident from this that brief heating to 850° produced no transformation it is not suggested that any firm conclusions regarding stability relations are to be drawn from this result.

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# DIFFERENTIAL THERMAL ANALYSES OF DAVIDITE

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## ABSTRACT

A specimen of a black radioactive mineral from Mozambique of a type recently described by Bannister and Horne (1950) has been examined by means of differential thermal analysis and  $x$ -ray diffraction. It is believed to correspond in essential features to the davidite from Olary, South Australia, as described by Mawson. The principal metallic elements in the Mozambique mineral are titanium, iron, uranium and chromium. Experimental data further confirm Mawson's original description of davidite as a distinct mineral species. The application of differential analysis to the study of metamict minerals is also suggested.

## INTRODUCTION

Davidite was described by Mawson (1906) as a black radioactive mineral occurring in a quartz-ilmenite-biotite lode south of Olary, South Australia. Later Crook and Blake (1910) concluded that davidite consisted of a mixture of ilmenite, magnetite, carnotite, possibly a little rutile and a silico-titanate of rare earths which might have been tscheffkinite, a conclusion with which Mawson (1916) failed to agree.

In July 1948 two specimens of a similar black radioactive mineral from Mavuzi, Tete district, Mozambique, Portuguese East Africa, were separately submitted to the mineralogical laboratory of Columbia University. These were massive in character, but contained chemical constituents suggestive of the constituents of crystals described as davidite by Mawson. The Mozambique mineral was found to yield thermal curves with significant exothermic reactions at about  $680^{\circ}\text{C}$  and  $800^{\circ}\text{C}$ . The mineral is judged to be metamict since unheated material fails to yield  $x$ -ray diffraction patterns while the patterns from heated samples\* are reproducible and distinctive. On polished surfaces the unheated material is isotropic.

Through the kindness of Professor Sir Douglas Mawson, of Adelaide, and Dr. C. F. Davidson of the Geological Survey of Great Britain, an opportunity has been offered to examine a specimen from Olary which contains small black grains of the type described by Mawson. This material yields a distinctive thermal curve with exothermic reactions corresponding to the reactions observed for the material from Mozambique and corresponds in  $x$ -ray diffraction effects.

Since this work was initiated,  $x$ -ray, chemical and crystallographic data on the Mozambique occurrence have been published by Bannister

\* Heated to  $1000^{\circ}\text{C}$  in air.

and Horne (1950). Data at hand are given for purposes of confirmation and to call attention to the possible application of differential thermal analysis to the study of metamict minerals.

#### ACKNOWLEDGMENTS

This study has been aided by Dr. Anton Gray, Chief Geologist of the Kennecott Copper Corporation, who supplied the original mineral from Mozambique and arranged for assistance in the laboratory examination. Appreciation is also expressed for the assistance of Dr. C. F. Davidson of the Geological Survey of Great Britain in providing a specimen of davidite from Olary. We are also indebted to Dr. P. M. Merritt, of Raw Materials Operations, A.E.C., for a second specimen from Mozambique. Mr. E. F. X. Lyden and Miss Jeanne Hutchinson, of Columbia University, have assisted in the x-ray diffraction measurements. Dr. D. L. Everhart of the Raw Materials Operations, A.E.C., has kindly offered suggestions in connection with the manuscript.

#### MINERAL FROM MOZAMBIQUE

The mineral from Mozambique is black with a vitreous to submetallic luster and a streak varying from brown to black. It is quite brittle and has a conchoidal fracture. The hardness is about 6, and the specific gravity is near 4.48. On the basis of measurement with a contact goniometer, Bannister and Horne (1950, p. 102) report that the mineral is hexagonal, ditrigonal pyramidal.

The hand specimen shows a platy cleavage but no crystal form was identified. Certain faces, however, suggest that the crystals are large, as illustrated by Bannister and Horne.

Small fragments of unheated material, minus 200 mesh, are often translucent to transparent, the transmitted light being a reddish brown, but both small and large fragments may be opaque. The mineral, when examined by means of polarized reflected light on a polished surface at a magnification of about 180, shows minute anisotropic inclusions, but the main mass is isotropic. The massive mineral appears to be essentially homogeneous as examined on a polished surface. Aside from gangue, impurities are estimated to account for a comparatively small amount of the mass examined.

A radiogram of the polished surface as illustrated in Fig. 1 shows some banding. The unexposed spots mark the position of minor nonradioactive inclusions.

Chemical determinations indicate that the mineral is primarily an oxide of titanium, iron, and uranium. Analyses shown in Table 1 have been reported by Bannister and Horne (1950, 1-7), Cooke (1916, 8) and

Ledoux and Co. (9-10). As pointed out by Bannister and Horne considerable chemical variation exists from sample to sample.

A partial spectrographic analysis of one of the mineral specimens indicates that columbium, bismuth, lead and aluminum are present in undetermined amounts. Scandium and neodymium may also be present. The portion of the mineral not indicated in the above chemical analyses may include these elements.

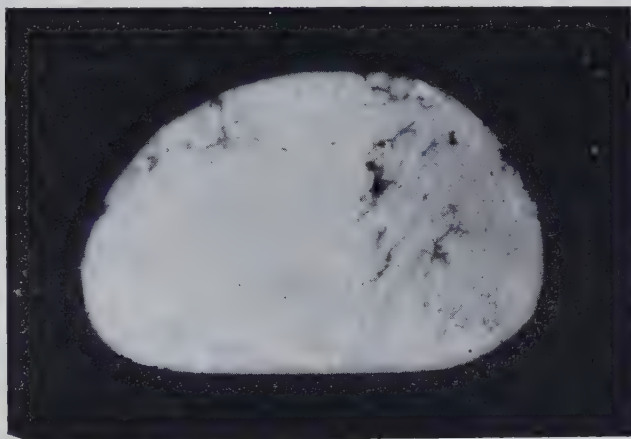


FIG. 1. Radiogram of a polished surface of davidite from Mozambique ( $\times 1\frac{1}{2}$ ). Dark areas represent non-radioactive impurities.

TABLE 1. CHEMICAL ANALYSES

	1	2	3	4	5	6	7	8	9	10
TiO <sub>2</sub>	54.5	51.00	60.5	36.70	47.40	45.80	51.30	54.3	49.22	47.91
Fe <sub>2</sub> O <sub>3</sub>	10.2	13.57	—	—	—	—	—	13.0	8.58	15.73
Cr <sub>2</sub> O <sub>3</sub>	0.17	3.23	4.8	3.42	4.62	4.21	4.86	4.6	2.97	—
V <sub>2</sub> O <sub>5</sub>	1.4	—	—	0.25	0.25	0.25	0.25		0.91	—
U <sub>3</sub> O <sub>8</sub>	9.8	7.10	7.5	5.50	7.85	8.00	8.02		9.19	5.26
FeO	16.5	12.37	27.0	21.90	23.20	22.40	24.90	16.0	17.96	10.36
ZrO <sub>2</sub>	0.4	3.30	—	—	—	—	—	—	—	—
(Ce, etc.) <sub>2</sub> O <sub>3</sub>	5.6	n.d.	—	3.10	3.60	4.52	4.24	8.3	n.d.	7.15
Na <sub>2</sub> O	0.15	1.72	—	—	—	—	—	—	—	—
CaO	0.3	1.00	—	12.40	5.00	4.60	3.00	1.5	—	—
ThO <sub>2</sub>	0.07	—	—	0.12	0.14	0.14	0.12	—	—	—
PbO	0.72	—	—	—	—	—	—	1.1	—	—
H <sub>2</sub> O	0.05	1.09	—	—	—	—	—	1.5	—	—
Insol.	—	—	—	2.90	5.20	3.00	1.40	—	—	—
Total	99.92	99.95	99.8	86.29	97.26	92.92	98.09	100.9	Partial	Partial

The mineral is not noticeably soluble in hot hydrochloric, nitric, or sulfuric acids, or a combination of the first two. In hot concentrated hydrofluoric acid it dissolves fairly rapidly, and a light green alteration product coats the surface. After short periods of immersion, a complicated etch pattern becomes visible.

Without prior heating, the mineral fails to yield an *x*-ray pattern with iron radiation even after exposure of 24 hours, but it gives a distinct and reproducible pattern after being heated to 1000° C, a common behavior for metamict minerals.

Characteristic thermal curves were obtained on apparatus described by Kerr and Kulp (1948). The curves exhibit satisfactory reproducibility (Fig. 2, curves 1, 2) at least in the upper temperature ranges. Exothermic peaks are developed at about 680° C, possibly due to oxidation, and there is a slight indication of a reaction in the vicinity of 900° C. *X*-ray patterns of samples after heating to 710° C give no distinct lines even after extended exposure, but patterns of samples heated to 830° C and 1020° C give groups of lines which are identical. The reversibility of the reactions may be indicated by recording the cooling curves. Since no peaks appear in the cooling curves to correspond to the reaction peaks of the heating curves, the reactions may be considered irreversible.

Thermal curves and *x*-ray patterns of the mineral have been compared with corresponding data for several well-known rare earth minerals (Figs. 3, 4). These curves are only exploratory but they indicate the possible utility of the method in the study of metamict minerals. As far as these comparisons go, the only mineral studied which approximates the thermal history of the Mozambique mineral is davidite. A comparison of the *x*-ray patterns of most of the minerals tested by thermal analysis confirms this evidence since davidite is the only mineral of the group found to have a pattern after heating which corresponds to that obtained from the heated Mozambique mineral. The strongest lines of the pattern from heated davidite are shown in Table 2 with the strongest lines of the pattern from one of the Mozambique specimens (Davidite 1).

#### DAVIDITE

As indicated above, davidite was described by Mawson (1906) as a black mineral occurring in cube-like crystals. A study by Crook and Blake (1910) purported to show that the mineral described by Mawson was not a unique mineral species but rather a mixture of ilmenite impregnated with magnetite, carnotite, possibly a little rutile, and a titanosilicate of rare earths which might have been tscheffkinitite. In a later paper Mawson (1916) pointed out that the material which formed the basis of the report by Crook and Blake contained no typical davidite that



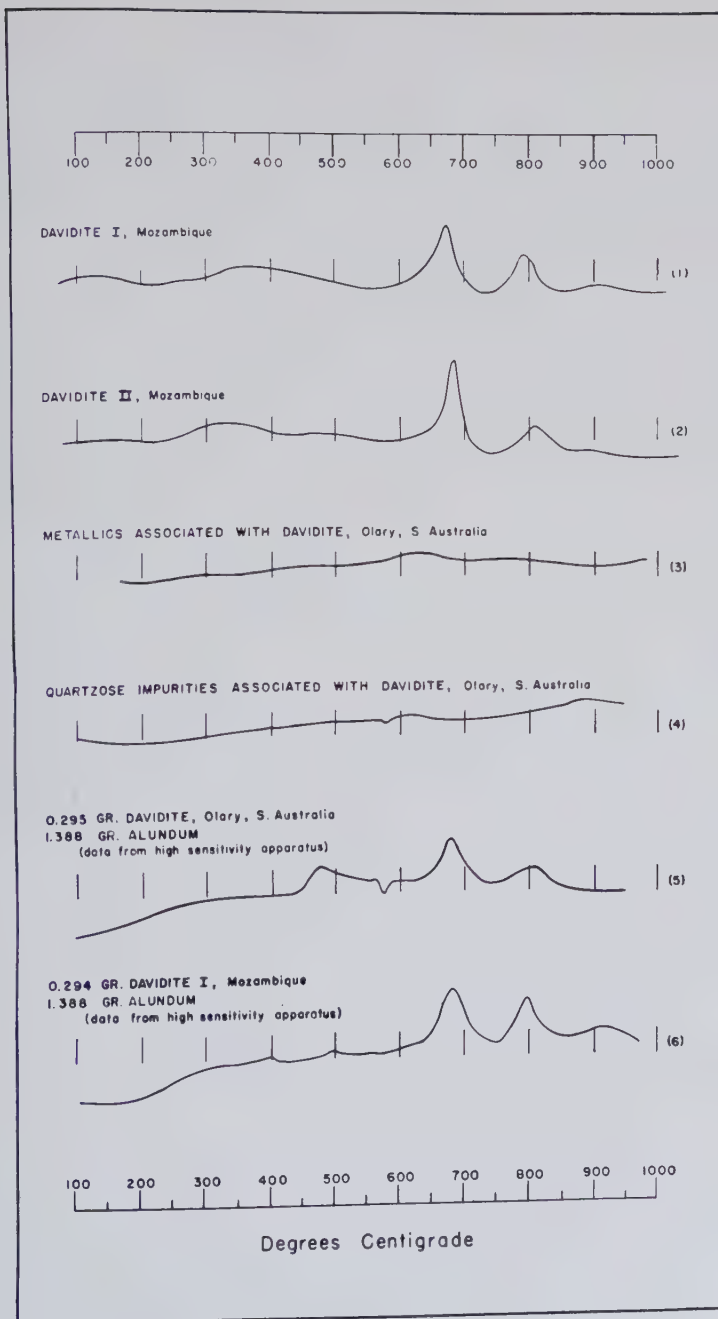


FIG. 2. Thermal curves of davidite specimens.

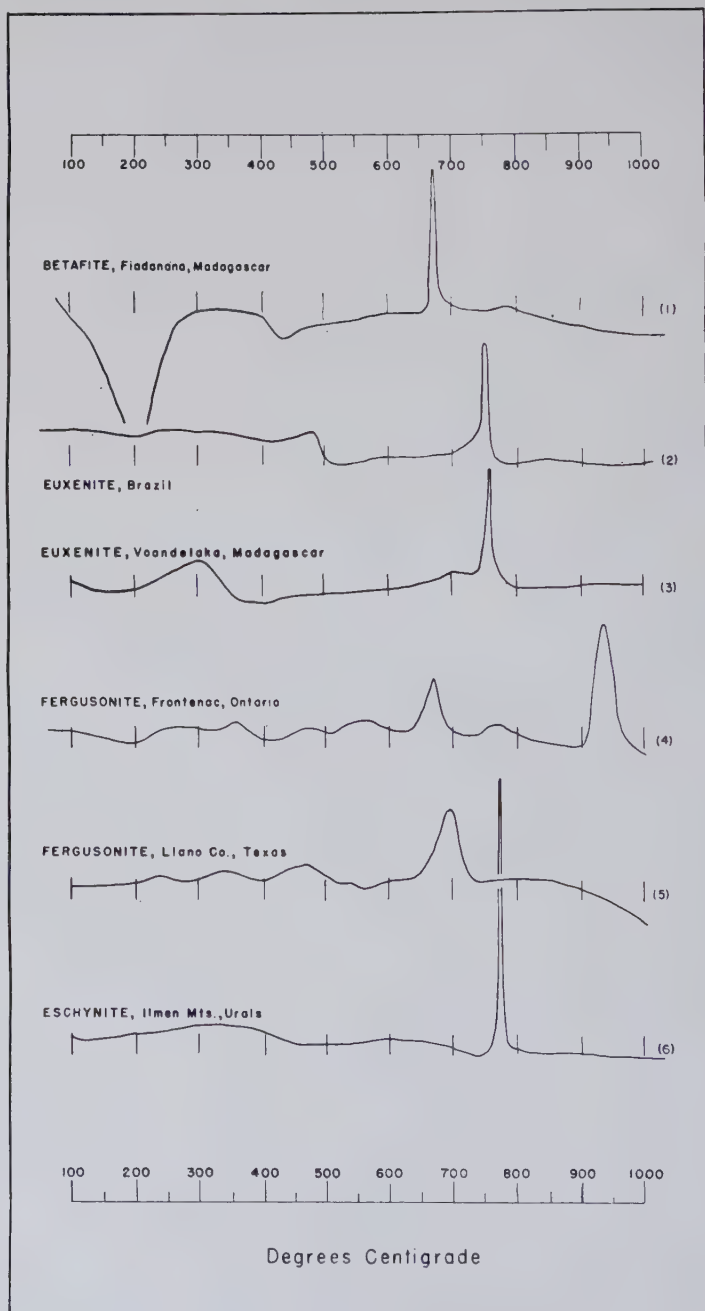


FIG. 3. Thermal curves of betafite, cuxenite, fergusonite and eschynite.

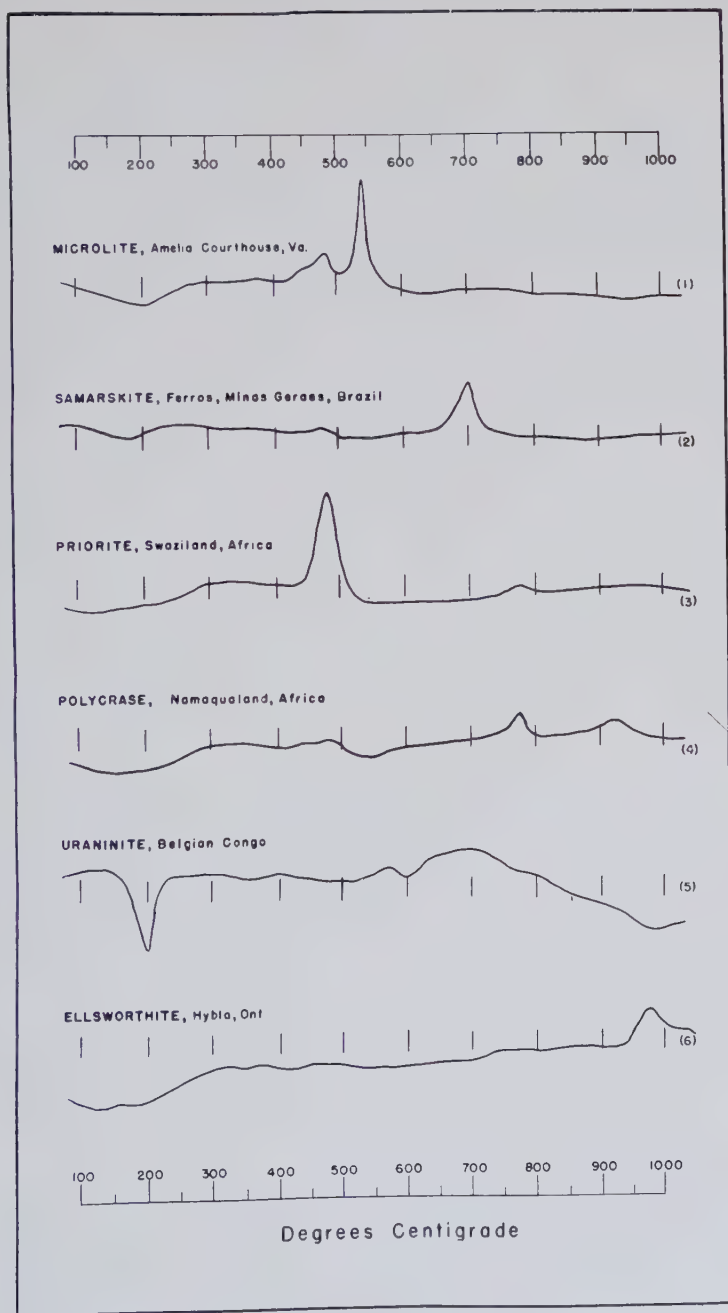


FIG. 4. Thermal curves of microlite, samarskite, priorite, polycrase, uraninite and ellsworthite.

TABLE 2. X-RAY DIFFRACTION DATA ON DAVIDITE

(After heating at 1000° C)

Cu—radiation; Ni—filter

Davidite, Mozambique				Davidite, Olary, S. Australia	
Specimen 2		Specimen 1		<i>d</i>	<i>Est. I</i>
<i>d</i>	<i>Est. I</i>	<i>d</i>	<i>Est. I</i>		
—		6.71	(2)	—	
—		5.16	(1)	—	
—		4.47	(2)	—	
—		4.15	(6)	—	
3.38	(7)	3.40	(9)	3.42	(6)
3.22	(7)	3.23	(8)	3.25	(6)
3.06	(6)	3.05	(8)	3.08	(3)
—		—	—	3.03*	
—		—	—	2.91*	
2.86	(9)	2.87	(10)	2.86	(10)
—		—	—	2.77*	
2.62	(3)	2.62	(3)	2.65	(2)
2.47	(8)	2.48	(8)	2.49	(7)
2.41	(1)	2.42	(3)	2.44	(3)
2.23	(6)	2.25	(8)	2.26	(7)
2.17	(1)	2.19	(3)	2.20	(4)
2.12	(4)			2.15	(1)
2.10	(4)	2.10	(2)	2.09	(1)
		2.03	(1)	2.04	(4)
1.95	(1)	1.96	(2)	1.97	(1)
1.90	(2)	1.91	(4)	1.92	(2)
1.83	(1)	1.84	(2)	1.85	(2)
1.79	(4)	1.80	(6)	1.81	(8)
1.76	(1)	1.78	(1)	1.78	(2)
1.69	(10)	1.70	(9)	1.71	(8)
				1.69	(8)
1.64	(1)			1.65	(1)
1.62	(1)			v. faint	
1.59	(9)	1.60	(5)	1.60	(9)
1.56	(1)	1.57	(1)	1.58	(2)
1.54	(1)	1.55	(1)	1.55	(2)
1.50	(2)	1.51	(3)	1.51	(1)
1.43	(9)	1.44	(7)	1.44	(9)
1.37	(1)	1.38	(4)	†	
1.12	(1)	1.12		†	
1.06	(1)	1.07	(2)	†	
0.90	(1)	0.90	(3)	†	
0.88	(1)	0.89	(2)	†	
0.86	(1)	0.86	(3)	†	
0.83	(1)	0.83	(3)		
		0.82	(1)		

\* Impurities.

† Present but faint.



could be observed with the naked eye. Since in other parts of the lode davidite occurs in the form of rough crystals, which are microscopically homogeneous, Mawson felt that the conclusions reached by Crook and Blake were not valid.

W. T. Cooke (1916) analyzed Mawson's material. The result of his analysis is shown in Table 1, together with the analyses of specimens from Mozambique. Material from Olary was secured from Mr. Hugh Ford, of New York. From *x*-ray data it is reasonable to assume that a large part of this sample may be composed of a mixture of ilmenite, magnetite and rutile, although the patterns are rather poor for such a mixture. The thermal curves of the material are inconclusive but could represent such a mixture.

One of the original specimens from which davidite was described was secured through the courtesy of Prof. Mawson and Dr. Davidson. The mineral occurs in bright grains embedded in part in a quartzose matrix and in part in a dark metallic mass. Carnotite coats the surface and mica is present in places. The metallic constituents, the quartz-bearing portion, and the davidite were separated as carefully as possible, and each part was subjected to thermal and *x*-ray analysis.

The metallic constituents associated with the bright black grains yield a somewhat indefinite thermal curve (Fig. 2, Curve 3). The low, broad peaks in the upper range are difficult to interpret. However, it is possible that these peaks are caused by small amounts of the material composing the bright black grains in a mixture with thermally inert minerals.

The light-colored portion of the gangue associated with the davidite gives the *x*-ray pattern of quartz while an admixture of the mineral with an inert material gives a thermal curve (Fig. 2, Curve 4) indicating an endothermic peak at about 573° C.

The bright black grains of the specimen were also subjected to both thermal and *x*-ray analysis. For the former procedure, the sample was mixed with alundum to increase its bulk and was heated in high-sensitivity thermal apparatus (Kulp and Kerr, 1949). The curve obtained is shown in Fig. 2, Curve 5. There are exothermic peaks at 680° C and 810° C, a broad exothermic peak at 435° C, and a small, sharp endothermic peak at 575° C. The endothermic peak is possibly due to quartz, but the remaining peaks seem significant of the dark mineral. These curves show that the black grains differ from the metallics with which they are associated. *X*-ray patterns of the grains confirm this conclusion. The unheated material fails to give an *x*-ray pattern with iron radiation after an eleven-hour exposure, but a pattern is obtained from material heated to 1000° C. The latter agrees in no respect with the pattern of the associated metallics.

X-ray diffraction measurements of the selected material from Olary and the two specimens from Mozambique are given in Table 2. The measurements are in approximate agreement with Bannister and Horne's measurements for material heated in air. Both, however, show the effects of impurities. Certain lines shown by the Olary material are missing in the patterns of the Mozambique specimens. This may be due to differences in exposure or to the presence of slight impurities in the Mozambique pattern causing additional lines. The agreement, however, is believed sufficient to justify the conclusion that the three patterns are representative of materials which are structurally the same.

These data support Mawson's contention that Crook and Blake (1910) based their observations not on the mineral which was originally used in describing the mineral davidite but on material of a different sort.

### CONCLUSIONS

(1) Davidite as described by Mawson is probably a distinct mineral and the specimen identified by Crook and Blake as a mixture appears to have been a different material.

(2) In general features, material from Mozambique corresponds to davidite as described by Mawson. The similarity in the properties of the two specimens lends support to the conclusion that davidite is a distinct mineral.

(3) It would appear that differential thermal analysis may be applicable to the identification of metamict minerals.

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# PEROVSKITE

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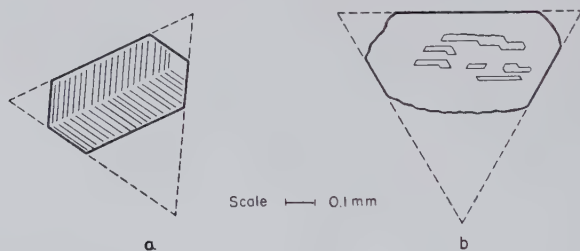
## ABSTRACT

Optical and x-ray study of perovskite from two new localities in California, and from Magnet Cove, Arkansas, and Vogtsburg, Germany, shows a unit cell edge double the current value. The new figure is:  $a_0 = 15.26 \pm .01 \text{ \AA}$  for the more ordinary perovskite, and somewhat greater for the variety dysanlyte:  $a_0 = 15.39 \pm .01 \text{ \AA}$ . All specimens showed multiple twin lamellae, parallel to the cube edge and also to the dodecahedron.

## CRESTMORE—1

Recently, one of the author's students found on the 910 level of the Commercial quarry at Crestmore, Riverside County, California, some fragments which contained scattered small octahedral crystals, amber to yellow in color. An examination of these proved them to be perovskite, and this, the first record of this mineral for California, was reported at the El Paso Meeting of the Mineralogical Society of America (1). The mineral occurs in the contact zone of the deposit, associated with nearly black octahedra of spinel, and an unidentified soft fibrous white mineral, probably a calcium silicate, interstitial to coarsely crystalline calcite. The perovskite is essentially normal calcium titanate, but with a perceptible amount of Zr, suggesting relationship to the mineral uhligite. Spectroscope analysis yields the following information: Large amount, Ca, Ti; % in units, Zr, Fe, Si (probably as impurity); % in tenths, Mg, Al; trace, Na, Sr, Mn. The presence of ordinary perovskite in a contact metamorphic deposit has not hitherto been reported, although dyasnanlyte is known under these conditions. The perovskite crystals range from a few tenths of a millimeter up to one or even two millimeters in diameter. In habit they are essentially octahedra, with sometimes small modifying cube faces. The octahedron faces are in general of very good quality, and measurement on the goniometer of selected crystals showed very close correspondence in position with the true isometric form. In four good measured crystals the rho angle varied from the theoretical by a maximum of  $21'$ , and in most cases much less than this. The phi angle was even closer, with a maximum variation of  $14'$ , and in one crystal the theoretical value was recorded, within limit of reading error, for all four faces of the measured half of the crystal. In none of these variations was there indication of a systematic deviation, such as Zedlitz (2) p. 268, reported for minute synthetic crystals. The cube faces were not in general of such good quality, but their position was in reasonable agreement with the theoretical.

Many of the crystals are equidimensional, but not infrequently some are flattened perpendicular to an octahedral axis. Such crystals, observed under the microscope, show multiple twin lamellae, with the junction lines running usually in two, and occasionally in three directions, at  $60^\circ$  to each other. Sometimes these directions bisect the angles of the octahedral face, indicating twinning on  $\{110\}$ . At other times the lines run parallel to the edges of the face, which could mean twinning either on  $\{110\}$  or  $\{100\}$ . In this case it would be possible to distinguish between the two possibilities by means of the universal stage. Some of the crystal faces, with proper illumination show a pattern of lines indicating twin lamellae, and one showed geometrically outlined "plateaus" on the surface. These are illustrated in the accompanying sketch (Fig. 1).



Natural crystal faces. a- striations b- "plateaus"

FIG. 1

A few crystals were ground down to thin sections, some parallel to the cube, some to the octahedron. Those on the cube face showed twin-lamellae parallel to the cube edge, as well as some diagonal ones. The cubic twin lamellae show at times a nearly centered optic axis figure with  $2V$  about  $90^\circ$ . Dispersion is prominent. Occasionally, as on some cube faces, a negative uniaxial figure was observed, not perpendicular to the cube, but with the center just at the edge of the microscope field. This effect may be produced by multiple cross lamellae, as suggested by Mallard (3) p. 149, as it appears in areas which do not show entire uniformity of optical direction, but have a wavy or vague extinction, clearly produced by several lamellae in the field of view. Bowman (4) p. 160 finds similar anomalies in crystals from the Tirol, and reports a positive acute bisectrix of small angle on the cube face.

#### CRESTMORE—2

More recently the author found another occurrence of perovskite at Crestmore. This also comes from the 910 level, Commercial quarry,



but differs in association and appearance from the first. The crystals are dark brown in color, not in general so well developed, although some octahedron faces and an occasional cube face were observed. They are closely associated with calcite, abundant pale greenish xanthophyllite and a light amber monticellite, and apparently crystallized earlier than these minerals.

#### SAN BENITO COUNTY

At the time the Crestmore occurrence was reported, the author was informed of a second California locality, near the headwaters of the San Benito River, near the benitoite Gem Mine, in San Benito County. The perovskite was found here by Mr. David Grigsby of Berkeley, who very kindly supplied the writer with material for study, as well as providing information regarding the occurrence. The mineral is found as black, highly lustrous cubic crystals, sometimes rather highly modified, and ranging in size from under a millimeter up to at least 0.5 cm. across. It is associated with black dodecahedral crystals of melanite garnet, in a greenish chloritic schist. One of the crystals, measured on the goniometer, showed, besides the cube, which roughly determines the outline, the following forms: {210}, {320}, {430}, {540}, {111}, {311}, and more doubtfully {14.1.0}, {13.1.0}, {310}. The shiny black aspect is purely superficial, for on crushing, the mineral is seen to be nearly colorless and transparent. Fragments and sections show typical multiple twin lamellae, with the twinning usually but not invariably parallel to the cube edge. Some of the broader lamellae show extremely fine, barely visible lamellae parallel to the larger ones. The lamellae show extinction parallel to the cube edge, and a nearly centered optic axis figure with  $2V=90^\circ \pm$ . Dispersion is pronounced, with the red brush showing more curvature than the blue, indicating a negative optical character with  $r < v$ .

Spectroscopic analysis is essentially parallel with that of the Crestmore mineral in spite of the wide difference in color and habit. The following is reported: Large amount, Ca, Ti; % in units, Zr, Fe; % in tenths, Mg, Al, Mn, Si; trace, Na, Sr.

#### DIMENSIONS OF THE UNIT CELL

The validity of the current value for the unit cell edge ( $a_0=7.55 \text{ \AA}$ ) was brought in question by examination of an x-ray powder photograph of the Crestmore perovskite taken by Professor W. J. McCaughey of the Ohio State University. This was made for purposes of identification and the film kindly given the writer by Dr. McCaughey. He noted on this film several faint lines which could not be indexed as pseudo-cubic,

using the old value  $a_0 = 3.83 \text{ \AA}$ . Barth (8) p. 204, 210, finds  $a_0 = 3.795 \text{ \AA}$  for perovskite, and  $a_0 = 3.826 \text{ \AA}$  for dysanallyte. The writer tried indexing these with the doubled value found by Levi and Natta (5) and Zedlitz (2) p. 259, but still could not get agreement. Accordingly a new photograph was taken of the Crestmore—1 material. This photograph showed many more lines than the previous one, and on trial it was found possible to index practically all of these on a cubic basis by using a still further doubled value of  $a_0$ . Crestmore—2 showed essentially the same lines as Crestmore—1. In consequence of this discovery a powder photograph of the San Benito perovskite was made, and proved to be practically identical in pattern and spacing with that from Crestmore. This agreement confirms the validity of the fainter lines of the pattern, since impurities in two such widely different occurrences would probably not be the same. In addition, both samples were very carefully selected under the binocular and almost completely free from foreign matter. The spectroscopic analyses also show the essential similarity of the two, and the agreement in  $x$ -ray patterns could have been predicted from this.

After this confirmation of the more complex character of the perovskite structure, it was thought desirable to see what differences in the pattern were present with important variation in composition. Accordingly, through the courtesy of the U. S. National Museum, specimens of dysanallyte were obtained from Magnet Cove, Arkansas, and from the Kaiserstuhl, Baden, Germany. The Magnet Cove mineral (U.S.N.M. 80431) presumably carries about 10%  $\text{Ta}_2\text{O}_5$  plus  $\text{Cb}_2\text{O}_5$ , if as is probable it corresponds to the analyzed material from that locality. The German specimen (U.S.N.M. R-5029) may be somewhat different, as published analyses vary rather widely in the  $\text{Cb}_2\text{O}_5$  content although all show absence of  $\text{Ta}_2\text{O}_5$ . Analyses of these two occurrences are listed in the following table.

These two specimens were crushed, hand-picked for purity, and similarly photographed and measured. Both showed essentially the same lines as the earlier ones, with comparable intensities, but with slightly different spacings. The German mineral showed considerable alteration to a black powdery substance, which could not be entirely separated from the clear material. This diminished the quality of the  $x$ -ray picture, but introduced no new lines.

The Magnet Cove specimen was black, somewhat corroded and pitted, and full of small white apatite prisms, which also appear in the lining of some of the cavities. Only the perfectly fresh material was picked out for the powder photograph. Unaltered parts of the crystal were transparent in very thin section, showing anisotropism and poorly defined twinning lamellae parallel to the cube edge; no interference figure could

	<i>Magnet Cove, Ark.</i>		<i>Vogtsburg, Kaiserstuhl, Baden</i>	
	1	2	3	4
CaO	33.22	25.60	21.63	23.51
MgO	0.74	—	0.02	—
(Y, Er, Tr) <sub>2</sub> O <sub>3</sub>	5.42	—	—	—
(Ce, La) <sub>2</sub> O <sub>3</sub>	0.10	2.80	3.32	3.08
Na <sub>2</sub> O	—	4.37	4.20	—
K <sub>2</sub> O	—	—	0.39	0.44
SiO <sub>2</sub>	0.08	2.21	0.29	0.33
TiO <sub>2</sub>	44.12	50.93	48.31	38.70
Cb <sub>2</sub> O <sub>5</sub>	4.38	4.86	16.12	25.99
Ta <sub>2</sub> O <sub>5</sub>	5.08	—	—	—
MnO	—	—	0.23	—
Fe <sub>3</sub> O <sub>4</sub>	0.73	—	—	—
Fe <sub>2</sub> O <sub>3</sub>	5.66	—	—	—
FeO	—	9.22	5.35	5.69
Al <sub>2</sub> O <sub>3</sub>	—	—	—	1.25
	99.53	100.22	100.88	100.28

1. F. W. Mar, *Am. J. Sci.*, **40**, 403-405 (1890); 2. Hauser, *Z. anorg. chem.*, **60**, 237 (1908); 3. & 4. Meigen & Hugel, *Z. anorg. chem.*, **82**, 242 (1913).

be seen. The Kaiserstuhl mineral, in its clear portions, also showed double refraction and poorly observable twinning lamellae. Hauser (6) called the mineral isotropic and believed that the Cb and Ce were present in mechanical impurities. It is interesting to note that Williams (7) p. 140 found minute (.05—.003 mm.) octahedra of perovskite in serpentine, and states that they are isotropic.

All powder photographs were taken with a North American Philips x-ray apparatus, using a camera of 57.3 mm. radius, Copper K $\alpha$  radiation with Ni filter using exposures of 8 hrs. at 28 KVP and 8 MA. Each film was calibrated from back reflections and measured to the nearest .05 mm. Spacings have been calculated in Å units. The value of  $a_0$  has been averaged from the measurements of a number of spacings both large and small and should for that reason be accurate to  $.01 \pm$  Å units. The values of  $a_0$  for the four localities are as follows:

Crestmore—1.	15.27 Å	Magnet Cove	15.38 Å
Crestmore—2.	15.29 Å	Kaiserstuhl	15.41 Å
San Benito	15.25 Å		

Study of the powder photographs shows very close correspondence with cubic spacings, although of course, since the mineral is anisotropic, it must be only pseudo-cubic. The deviation of the cell from a cube must

be very small indeed, as in only two lines is there a suggestion of doublets, whose presence would be a very delicate indication of differences in the lengths of the cell edge. These appear at spacings 1.56–1.55, Å (448), with intensity 7 and 7, and at 1.018–1.023, Å (4.8.12) with intensities 4 and 1, respectively. The latter was noted by Zedlitz (2) p. 259 as diffrused, with equal intensities (10–10), indexed as (246).

The following table gives the lists of spacings and estimated intensities of the lines for each locality. (*See next page.*)

### CONCLUSIONS

From the data at hand, the similarity of pattern for all occurrences and the close agreement with a pseudo-cubic structure, it seems most probable, as has been suggested, that perovskite crystallizes in truly isometric form, but inverts with lowering temperature to the observed structure, whose true symmetry remains uncertain, but is clearly non-isometric optically, though it appears to be practically cubic structurally. The pseudo-cubic unit cell increases in size with the increase in Ta and Cb content, ranging as shown from 15.25 to 15.41 Å units. No attempt has been made to determine the distribution of atoms in this structure, owing to its complexity and the apparent improbability of getting a single crystal for *x*-ray study.

### ACKNOWLEDGMENTS

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4. BOWMAN, H. L., On the structure of perovskite from the Burgumer Alp. Pfischthal, Tyrol: *Min. Mag.*, **15**, 156–176 (1908).



TABLE 2. POWDER PHOTOGRAPH DATA ON PEROVSKITE

Copper radiation,  $d/n$  in Å units

No.	Indices	San Benito		Crestmore-1		Crestmore-2		Magnet Cove		Kaiserstuhl	
		$d/n$	$I$	$d/n$	$I$	$d/n$	$I$	$d/n$	$I$	$d/n$	$I$
1	004	3.81	4	3.82	3	3.81	2	3.84	4	3.84	3
2	024	3.41	1	3.42	1	3.42	$\frac{1}{2}$	3.43	$\frac{1}{2}$	3.54?	1
										2.30?	1
3	015, 134	2.98	1	2.99	1	3.01	$\frac{1}{2}$	3.00	$\frac{1}{2}$	3.01	1
4	044	2.70	10	2.70	10	2.70	10	2.72	10	2.72	10
5	006	2.54	$\frac{1}{2}$	2.56	$\frac{1}{2}$	2.56?	$\frac{1}{2}$	2.58	$\frac{1}{2}$	2.54	$\frac{1}{2}$
6	026	2.41	1	2.41	1	2.42	$\frac{1}{2}$	2.44	$\frac{1}{2}$	2.43	$\frac{1}{2}$
7	226	2.30	3	2.30	1	2.30	1	2.32	2	2.32	$\frac{1}{2}$
8	444	2.20	3	2.21	2	2.21	1	2.24	$\frac{1}{2}$	2.22	1
9	046	2.12	2	2.12	1	2.12?	$\frac{1}{2}$	2.14	$\frac{1}{2}$	2.14	$\frac{1}{2}$
10	246	2.04	$\frac{1}{2}$	2.04	$\frac{1}{2}$	2.05	$\frac{1}{2}$	2.06	$\frac{1}{2}$	2.11	$\frac{1}{2}$
11	008	1.91	9	1.91	9	1.91	7	1.93	8	1.93	9
12	028, 446	1.85	$\frac{1}{2}$	1.86	1	1.86	$\frac{1}{2}$	1.88	$\frac{1}{2}$	1.87	$\frac{1}{2}$
13	048	1.71	1	1.71	1	1.72	$\frac{1}{2}$	1.73	1	1.73	1
14	119, 357	1.67	1	1.67	1	1.68	$\frac{1}{2}$	1.69	$\frac{1}{2}$	1.69	$\frac{1}{2}$
										1.67	$\frac{1}{2}$
15	139	1.56	7	1.56	7	1.57	5	1.57	6	1.57	5
16	448	1.55	7	—	—	—	—	—	—	—	—
17	359	1.42	$\frac{1}{2}$	1.43	$\frac{1}{2}$	—	—	—	—	—	—
18	369, 1.2.11, 1.5.10	1.356	$\frac{1}{2}$	—	—	—	—	—	—	—	—
19	088	1.349	6	1.35	5	1.35	3	1.36	3	1.36	3
20	2.3.11, 279, 3.5.10, 677	1.32	$\frac{1}{2}$	—	—	—	—	—	—	—	—
21	0.4.11, 1.6.10, 388	1.30	$\frac{1}{2}$	—	—	—	—	—	—	—	—
22	2.6.10	1.29	$\frac{1}{2}$	1.29	$\frac{1}{2}$	—	—	—	—	—	—
23	0.4.12	1.21	5	1.21	4	1.21	2	1.22	3	1.22	3
24	199	1.19	$\frac{1}{2}$	—	—	—	—	—	—	—	—
25	0.2.13, 2.5.12, 3.8.10, 4.6.11	1.16	$\frac{1}{2}$	—	—	1.147?	$\frac{1}{2}$	—	—	—	—
26	1.3.13, 779, 3.7.11	1.14	$\frac{1}{2}$	1.14	$\frac{1}{2}$	—	—	—	—	—	—
27	3.9.10	1.11	1	1.11	1	1.12	$\frac{1}{2}$	1.12	1	1.12	$\frac{1}{2}$
28	0.7.12, 6.6.11	1.01	1	1.01	1	1.11	$\frac{1}{2}$	1.11	1	1.11	$\frac{1}{2}$
29	0.2.14, 0.10.10, 6.8.10	1.08	$\frac{1}{2}$	—	—	—	—	—	—	—	—
30	1.9.11, 3.5.13	1.07	$\frac{1}{2}$	—	—	—	—	—	—	—	—
31	1.8.12, 2.3.14, 2.6.13, 3.10.10, 4.7.12, 889	1.06	$\frac{1}{2}$	—	—	—	—	—	—	—	—
32	1.5.14, 1.10.11, 2.7.13	1.023	1	1.024	1	—	—	1.035	$\frac{1}{2}$	1.035	$\frac{1}{2}$
33	4.8.12, 0.0.15, 0.9.12, 2.5.14, 2.10.11, 5.10.10	1.018	4	1.019	3	1.021	2	1.027	2	1.026	1
34	0.0.16, 2.5.15, 2.9.13, 3.7.14, 6.7.13	.9554	1	.9563	$\frac{1}{2}$	.956	$\frac{1}{2}$	.9643	$\frac{1}{2}$	.9638	$\frac{1}{2}$
35	0.3.16, 0.11.12, 2.6.15	.9362	$\frac{1}{2}$	—	—	—	—	—	—	—	—
36		.9312	$\frac{1}{2}$	—	—	—	—	—	—	—	—
37		.9069	$\frac{1}{2}$	—	—	—	—	—	—	—	—
38		.9043	$\frac{1}{2}$	—	—	—	—	—	—	—	—
39		.9011	4	.9005	2	.9012	2	.9070	2	.9078	2
40		.8549	2	.8560	2	.8557	1	.8623	2	.8601	$\frac{1}{2}$
41		.8525	1	.8536	1	.8527	1	—	—	.8588	$\frac{1}{2}$
42		—	—	—	—	—	—	—	—	.8258	$\frac{1}{2}$
43		.8188	$\frac{1}{2}$	.8188	$\frac{1}{2}$	—	—	—	—	.8186	$\frac{1}{2}$
44		—	—	—	—	—	—	—	—	.8258	$\frac{1}{2}$
45		.8129	2	.8134	2	.8126	1	.8190	2	.8186	$\frac{1}{2}$
46		.8108	1	.8118	1	—	—	—	—	—	—
47		.7841	1	.7849	1	—	—	—	—	—	—
48		.7822	1	.7824	1	.7826	$\frac{1}{2}$	.7841	$\frac{1}{2}$	—	—
49		.7787	$\frac{1}{2}$	.7790	$\frac{1}{2}$	—	—	—	—	—	—
50		—	—	.7768	$\frac{1}{2}$	—	—	—	—	—	—
51		—	—	—	—	—	—	.7753	$\frac{1}{2}$	—	—
52		—	—	—	—	—	—	.7747	$\frac{1}{2}$	—	—

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# OBSERVATIONS ON TWINNING OF PLAGIOCLASE IN METAMORPHIC ROCKS

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## ABSTRACT

Metamorphic plagioclase in general is characterized by: (1) comparative rarity of twinning; (2) prevalence (in low-grade schists) of simple twins consisting of few subindividuals; (3) predominance of albite and pericline twins, Carlsbad twins being subordinate; (4) absence of complex twin combinations. Comparison with twinning of plagioclase of igneous rocks and of migmatites yields evidence tending to support magmatic origin of most granites and diorites.

## INTRODUCTION

Petrographic literature of the last twenty years includes a number of studies on occurrence, nature, and origin of twinning in plagioclase of igneous rocks (e.g., Coulson, 1931; Barber, 1936; Chapman, 1936; Emmons and Gates, 1943). Corresponding accounts of twinning in metamorphic plagioclase are few and meager, a notable exception being the observations of Phillips (1930) on plagioclase of the Green Bed group of the Scottish Dalradian schists. The purpose of this note is to record some of my own observations regarding the types of twinning commonly encountered in plagioclase of various metamorphic rocks and to draw attention to certain consistent differences in twinning between metamorphic and igneous plagioclase. Such differences, if confirmed by others working in this field, may possibly have some bearing on the vexed problems connected with the origins of granitic and dioritic rocks.

## TWINNING IN METAMORPHIC PLAGIOCLASES

The generalizations which follow are based partly on recorded observations of other petrographers, partly on my own experience. The latter involves determination of twin laws by standard universal stage procedure (Turner, 1947) in all cases.

(1) Prevalence of untwinned plagioclase in metamorphic rocks of all types is too well known to merit further comment. There is scattered evidence in petrographic literature suggesting that twinning of plagioclase is more frequent in rocks of moderate to high metamorphic grade than in albite-bearing schists of the greenschist facies. Thus Phillips (1930, pp. 244, 245) records increasing abundance of twinned grains of albite in passing from the chlorite zone to the biotite zone of the Scottish Dalradian schists. My own observations confirm this general tendency:

(a) In even-grained greenschists and quartz-albite-muscovite-chlorite schists within the chlorite zone of regional metamorphism in New Zealand, untwinned grains of albite are very common in most thin sections and twinned grains typically are rare or absent. In porphyroblastic albite schists from the same region, simple twinning of albite is distinctly more common, though the majority of the porphyroblasts still are untwinned. The same generalization applies to suites of albite-quartz-piedmontite schists and porphyroblastic albite-chlorite schists of the Besshi series, Japan (cf. Suzuki, 1930) and to various German and Alpine greenschists which I have examined.

(b) In albite-bearing glaucophane schists from the Franciscan of California (believed to belong to the greenschist or the albite-epidote-amphibolite facies) albite seems to be somewhat more commonly twinned than in most other greenschists. The albite here tends to be porphyroblastic, and the twinned coarse grains in most cases consist of two to four subindividuals of nearly equal size.

(c) In amphibolites and quartz-biotite-oligoclase schists of the amphibolite facies in New Zealand (Westland; Manopouri), plagioclase ranging from  $An_{20}$  to  $An_{45}$  commonly shows lamellar twinning. In individual sections between 10% and 50% of the grains show obvious twinning.

(d) Preponderance of grains with lamellar twinning over untwinned grains has been observed in a number of hornfelses of the amphibolite facies (e.g., Bluff, New Zealand; Engel Mine, California) and in German pyroxene granulites.

(2) There seems to be no general correlation between abundance of twinning in metamorphic plagioclase and degree of deformation experienced by the enclosing rock. The most abundant twinning I have seen is in undeformed hornfelses and metasomatic rocks; and Goldschmidt (1911, pp. 293, 295) records plentiful albite twinning in oligoclase and andesine of the Oslo hornfelses. Moreover, the albite porphyroblasts of the post-tectonic stage in New Zealand schists are twinned to just the same extent as are rotated porphyroblasts of paratectonic origin. On the other hand discontinuous lamellar twinning has been observed at margins of residual large albites in strongly sheared and granulated albite-quartz rocks occurring as dikes in California serpentinites. Here metamorphism is local and strictly cataclastic.

(3) Various writers have contrasted the simple twinning of metamorphic plagioclase with the characteristically complex twinning of plagioclase in igneous rocks (e.g., Phillips, 1930, p. 247; Harker, 1932, p. 213). In the great majority of metamorphic rocks which I have examined, twinned grains of plagioclase consist of few subindividuals, and only one twin law is represented in most grains. This contrasts very strikingly



with the variety and complexity of twinning exhibited by igneous plagioclase and with the large number of lamellae that occur in many grains in igneous rocks. There are, however, certain exceptions. In pyroxene granulites and in certain hornfelses of relatively high grade, grains of plagioclase may consist of many closely-spaced lamellae, though there is still a marked tendency for only one twin law to be represented in any grain. In amphibolites of igneous origin, coarse plagioclase (in some cases retaining relict idiomorphic outlines) is liable to show twinning just as complex as that of igneous plagioclase—albite-Carlsbad-pericline combinations especially. The twinned condition and crystal habit of such plagioclase are considered to be relict and afford good evidence of igneous parentage of the amphibolite in which they are observed.

(4) Phillips (1930, p. 247) records the percentage frequencies of various types of twinning observed by him in plagioclase of schists belonging to the Dalradian Green Bed group as follows: albite 60%, pericline (mainly in oligoclase and andesine) 17%, Carlsbad 16%, other laws 7%. My observations confirm the great prevalence of albite and pericline twinning in metamorphic plagioclase (cf. also Goldschmidt, 1911, pp. 292–300; Ambrose, 1936, pp. 262, 264, etc.); but I would rate pericline twinning as being more frequent and Carlsbad twinning much less frequent than the figures given by Phillips would indicate. Some further generalizations in this connection may be noted:

(a) Albite porphyroblasts in greenschists and related rocks of low to moderate metamorphic grade rather commonly consist of two twinned subindividuals of approximately equal size with  $\{010\}$  as composition plane. These have been identified as Carlsbad twins by most writers (e.g., Knopf and Jonas, 1929, p. 29; Hietanen, 1941, p. 102; Turner and Hutton, 1941, p. 224). I have examined many sections of porphyroblastic albite schists from New Zealand, Japan, and California and have found in every case that the majority of these simple twins are actually composed of two subindividuals twinned on the albite, not the Carlsbad, law. Carlsbad twins are also present in some rocks but always in subordinate numbers. Carlsbad and albite twinning in pure albite are optically indistinguishable from each other. Since  $X$  is almost parallel to the composition plane  $\{010\}$  and at the same time is almost perpendicular to the crystal axis  $[001]$ , there are two possible solutions to the problem of identifying the twin axis from the respective positions of  $X$ ,  $Y$  and  $Z$  in each of the twinned subindividuals. Either  $[001]$  or  $\perp\{010\}$  as twin axis will satisfy the optical data within the limits of probable experimental error. However, the ambiguity may be resolved if the  $\{001\}$  cleavage plane is measured in both subindividuals; for the angle between the two  $\{001\}$  poles is  $7^\circ$  in the case of albite twins,  $53^\circ$  in Carlsbad twins. Even

without a universal stage the twin axis of suitably oriented albite porphyroblasts may be identified microscopically as  $\perp \{010\}$  from the fact that the transverse  $\{001\}$  cleavage continues across both subindividuals with but slight deflection where it crosses the composition plane. If  $\{001\}$  cleavage is clearly visible in one half of a section of a Carlsbad twin, it is invisible in the adjoining half—though by appropriate tilting on a universal stage it may be found and identified in most cases.

(b) My experience agrees with that of Phillips (1930, pp. 247, 248) that albite twinning greatly predominates over other types of twinning in sodic plagioclase ( $An_0$  to  $An_7$ ) of rocks within the greenschist facies. There are other records, however, of predominant pericline twinning in nearly pure albite of such rocks (e.g., Ambrose, 1936, p. 262). With certain exceptions (e.g., the pyroxene granulite and the hornfels noted at the bottom of Table 1), pericline twinning of plagioclase is at least as common as albite twinning in rocks of higher metamorphic grades. Some illustrative examples, from my own measurements, are appended in Table 1.

TABLE 1: TWIN LAWS FOR PLAGIOCLASE OF METAMORPHIC ROCKS, MAINLY IN AMPHIBOLITE FACIES

Rock		Plagioclase	Number of measured twinned grains		
			Albite twin	Pericline twin	Combined albite-pericline twin
Amphibolites,	2461	$An_{24}$	8	6	1
Lake Manopouri,	7512	$An_{20-25}$	8	7	2
New Zealand	8014	$An_{33-38}$	12	24	4
Biotite-plagioclase schists	7531	$An_{20-25}$	—	3	—
Westland, New Zealand	7533	$An_{29-33}$	6	9	2
Almandine-mica schists,	22	$An_{30}$	—	3	—
European Alps	24	$An_3$	—	3	—
Plagioclase-garnet-epidote hornfels, Engel Mine, California	E64	$An_{75-80}$	—	10	—
Plagioclase-diopside hornfels, Bluff, New Zealand	7488	$An_{45}$	10	—	—
Pyroxene granulite, Germany	314	$An_{50-55}$	12	—	2

(c) Albite ( $An_{0-5}$ ) of Californian glaucophane schists commonly shows simple or very coarsely lamellar twinning on the albite law. Pericline twinning is generally lacking. I have seen no cases of undoubted Carlsbad twins in these rocks.

(5) There are many records of widely prevalent lamellar albite twinning in albite and oligoclase porphyroblasts formed by soda metasomatism. Becke (1913, pp. 124, 125) considered the interrupted blocky {010} twinning of "chessboard albite" to be a criterion of replacement of original potash feldspar by albite of this type (cf. also Anderson, 1937, pp. 62, 63). Goldschmidt (1911, pp. 301, 303, 305) has described "chessboard albite" as a constituent of various metasomatic rocks, including albite veins and impregnated skarns; but he states that in his experience this type of plagioclase does not occur in "normal contact rocks formed without introduction of material." Details of twinning are not recorded in most of the numerous accounts of feldspathized porphyroblastic albite and oligoclase gneisses occurring in migmatites adjacent to granitic bodies. From such data as are available (e.g., Goldschmidt, 1921, pp. 81, 82; Read, 1927, p. 338; Anderson 1934, p. 386, figs. 6, 7) it would seem that lamellar twinning on one law (probably albite law) is common in metasomatically formed sodic plagioclase. There are also references (e.g., Koch, 1939, p. 71) to occurrence of simply twinned oligoclase porphyroblasts in metasomatically affected rocks of this type. Complex combinations of albite, Carlsbad and pericline twinning in albite of sodic granites is probably a relict feature inherited from originally more calcic igneous plagioclase now replaced by albite.

#### INTERPRETATION

Plagioclase of schists and hornfeldes differs in a number of respects from plagioclase of undoubtedly igneous rocks as regards twinning phenomena:

- (1) Absence or rarity of twinning in many groups of rocks.
- (2) Prevalence, especially in low-grade schists, of simple twins consisting of a few (in many cases only two) subindividuals. Note, however, that in some sodic granites also simple albite twins of two subindividuals may occur.
- (3) Lack of variety in types of twin commonly represented; albite and pericline twins greatly predominate, Carlsbad twins are much rarer, other types (including complex combinations) are very rare; even albite-pericline combinations in one crystal are infrequent.
- (4) Frequent development, and in some rocks great preponderance, of pericline twinning, even in sodic plagioclases ranging from  $An_{10}$  to  $An_{30}$ .

There are exceptions to all of these rules. But their general validity is striking in view of the great range of composition and physical conditions of origin represented by metamorphic rocks. Reference to the detailed accounts of Duparc and Reinhard (1924, pp. 8-10), Coulson (1931), Barber (1936) and Chapman (1936) will make obvious the generally contrasted twinning behavior of igneous plagioclase.

It seems likely that the differences noted above may reflect generally prevalent differences in the respective physical conditions of magmatic and metamorphic crystallization. It is possible, for example, that twinning behavior, as well as crystal habit and the nature of the crystal boundaries, is affected differently by metamorphic crystallization of plagioclase in an essentially solid medium and by magmatic crystallization in a liquid medium. Temperature may well exert an even more important influence. Metamorphic temperatures in general are lower than magmatic temperatures. It is now known that sodic plagioclase ( $An_0$  to  $An_{35}$ ) inverts from a high- to a low-temperature form at temperatures a little below  $700^\circ\text{C}$ .; and it has been suggested (Tuttle and Bowen, 1950, p. 583) that "the nature of the twinning should certainly be different when the crystals are grown below the inversion, as compared with that developed when they are inverted from the high-temperature modification." Much of magmatic crystallization must take place above the inversion temperature, and most if not all metamorphic processes must be governed by temperatures considerably below it. Moreover, the optical properties of metamorphic plagioclase consistently conform to "low-temperature optics," rather than to the "high-temperature optics" now recognized (e.g., Barber, 1936, pp. 247-249; Oftedahl, 1948, pp. 10-15) as characteristic of phenocrysts in volcanic rocks. According to the French theory of twinning (Donnay, 1943) differences in twinning behavior of similar minerals are much more probably due to differences in space-lattice structure than to direct influence of external conditions such as temperature.

Plagioclase of porphyroblastic albite and oligoclase schists in migmatite areas seems, from such records as are available, to resemble metamorphic rather than undoubtedly igneous plagioclase as regards twinning. That of most granites, grandiorites, and diorites which I have examined shows the profusion and great variety of twinning typical of igneous plagioclase as developed in phenocrysts of volcanic rocks. Especially characteristic is the common appearance of the Carlsbad-albite combination, and the less frequent but still by no means rare occurrence of twins on Manebach and Ala laws. All of these are typically unrepresented or rare in plagioclase of metamorphic rocks. This is one more piece of evidence suggesting that the evolution of most granites, granodiorites,

and diorites involves crystallization of feldspar from a magmatic liquid (silicate-melt phase); and that the porphyroblasts of sodic plagioclase in many migmatitic schists and gneisses are products of metasomatism (a phase of metamorphism) in essentially solid rocks permeated by aqueous fluids introduced from igneous or other sources.

Much has been written on the problem of primary origin of plagioclase twins during crystal growth, versus secondary origin by deformation of the fully grown crystal. Most of the discussion centers around observations on twinning in igneous plagioclase. Barber (1936, pp. 256-258), from detailed observations on a wide range of plagioclases, found that there is a marked tendency for the composition plane of lamellar albite twins to be a vicinal face inclined to  $\{010\}$  at an angle of  $\frac{1}{2}^\circ$  to  $3^\circ$ . From this and from consideration of external morphology he concluded that it was possible to recognize "many examples of twinning, including albite and pericline twinning, which it is considered must be primary." He found no conclusive evidence of secondary twinning in the material which he examined. Donnay (1940, 1943) explained the close relation, observed by many petrographers, between composition of plagioclase and mean width of albite twin lamellae, by assuming that twinning of plagioclase is a phenomenon of crystal growth and is controlled mainly by the geometry of the space lattice (which varies with variation in composition). The opposite view, that lamellar twinning of plagioclase is essentially secondary, has been stated by Emmons and Gates (1943) on the evidence of microscopic texture of igneous rocks. The observations on metamorphic plagioclase recorded in this paper support in two respects the view that much twinning in plagioclase is primary:

(1) Prevalence of simple albite twins, consisting of only two or three subindividuals of equal size, in almost pure albite of low-grade schists, confirms Donnay's (1940, p. 584) prediction that "in the short range from oligoclase to albite, one should expect a rapid widening of the lamellae, to such an extent that for pure or almost pure albite, twinning [on the albite law] may cease to be polysynthetic at all."

(2) In plagioclase of schists with strongly developed tectonite fabrics, resulting from continuous deformation proceeding simultaneously with crystallization, lamellar twinning is on the whole much less generally developed than in phenocrysts of volcanic rocks.

#### POSTSCRIPT—M. GORAI'S OBSERVATIONS ON TWINNING ON PLAGIOCLASE

Since this paper was accepted for publication, Dr. K. Yagi drew my attention to a recent important contribution to the same problem by



M. Gorai.\* Gorai has made a statistical study (based on several thousand universal-stage determinations) of the relative abundance of various kinds of twins in plagioclase of common igneous and metamorphic rocks, and has reached the following conclusions:

(1) Plagioclase twins commonly observed in volcanic and many plutonic rocks fall into two groups, both typically well represented in rocks of these classes: *C-twins*, including Carlsbad, Carlsbad-albite, and the much rarer Manebach, Baveno, Ala, and albite-Ala types; *A-twins*, including albite and pericline twins (and acline, which in plagioclase of intermediate composition is indistinguishable from pericline). In all undoubtedly igneous rocks untwinned plagioclase is subordinate to twinned plagioclase. These generalizations are demonstrated statistically by plotting, for each rock examined, the relative abundance of grains of three types (untwinned, A-twins and C-twins) on a triangular UAC diagram.

(2) In schists and hornfelses of undoubted metamorphic origin, only A-twins are commonly developed. In some rocks untwinned crystals greatly predominate; but in other rocks the majority of the grains may be twinned. C-twins are absent or inconspicuous in all cases.

(3) Development of C-twins is controlled partly by crystallization from a melt phase but apparently is influenced too by composition of plagioclase, in that C-twins seem to be more plentiful in calcic than in sodic plagioclase of volcanic rocks.

(4) Relative abundance of untwinned grains, A-twins, and C-twins in granites in some cases corresponds to that typical of igneous rocks; but in others, exemplified by granitic rocks of certain migmatites and tonalite-gneiss contact zones in Japan, the statistical pattern of plagioclase twinning is identical with that of metamorphic rocks. The type of twinning shown by plagioclase of granitic rocks is therefore considered to be a valuable criterion by which metasomatic granites can be distinguished from granites of magmatic origin.

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# TAYLORITE, MASCAGNITE, APHTHITALITE, LECONTITE, AND OXAMMITE FROM GUANO

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## ABSTRACT

The original type specimen of taylorite is believed located. It is an ammonian arcanite, belonging to the isomorphous series arcanite—mascagnite,  $K_{2-x}(NH_4)_xSO_4$ , with  $x$  near 0.35, according to a new analysis.  $2V = (-)$  small,  $N_x = 1.5007$ ,  $N_y = 1.5034$ ,  $N_z = 1.5048$ ; X-ray powder diffraction data in Tables 1 and 2. Mascagnite and arcanite were not found in the guano studied. Ammonian apthitalite predominates in a fossil penguin egg analyzed by Mrs. Setlow. Chemical, optical, and x-ray data in Tables 4 and 5;  $N_o = 1.4998$ ,  $N_e = 1.5026$ . Lecontite from the type locality, labelled by Taylor, was studied by x-ray methods (Table 6). Refractive indices  $1.495 \pm .010$ . Oxammite is ammonium oxalate monohydrate (not dihydrate), according to a new analysis (Table 7). This proved similar (Table 8) to oxammite from a specimen that is as nearly identical with Shepard's type specimen as any that probably exists.

## INTRODUCTION

During the preparation of a monograph on guano in the Survey of Contemporary Knowledge of Biogeochemistry, Professor G. E. Hutchinson of Yale University wished to have some specimens from guano deposits examined mineralogically. It soon became evident that certain problems needed further study; this report is the result. The minerals taylorite, apthitalite, glaserite, mascagnite, arcanite, lecontite, and oxammite have all been reported as occurring in guano, and several of these were found in the specimens studied, but their published descriptions were in some cases inaccurate. A comprehensive study of the guano specimens available was therefore undertaken not only to determine their components but also to characterize or re-describe certain ones.

## ACKNOWLEDGMENTS

Professor G. E. Hutchinson's work in assembling suitable specimens actually originated this study. He personally examined guano specimens in the collections of the American Museum of Natural History, of Columbia University, and of the Philadelphia Academy of Natural Sciences, obtaining valuable information and specimens at each institution. These specimens, together with ones from subfossil birds originally presented to the Peabody Museum of Yale University by Shepard (1870) from a boatload of guano that docked in Carolina that year, and several specimens from the Brush Mineral Collection of Yale University, constitute the material here described. The cordial cooperation of the several museums is acknowledged with great appreciation. X-ray and optical tests

were made with equipment provided by the trustees of the George Sheffield fund, and certain other funds of Yale University. Special thanks are due Professor C. Frondel of Harvard University for the pre-publication loan of his 1950 manuscript on certain sulfates. Thanks are due Mr. V. T. Bowen, Mr. T. Sippel, and Mrs. Jane K. Setlow for analyses.

### METHODS OF STUDY

Some specimens were identified by chemical analysis, most by *x*-ray powder diffraction and optical data; in all cases the refractive indices and *x*-ray powder diffraction data were eventually obtained. Optical studies were carried out mainly by the immersion method at room temperature, with white light. The accuracy of such results is  $\pm 0.005$ . Critical specimens were studied by the Emmons double-variation method (1929, p. 415), and accuracy in such cases is probably about  $\pm 0.0004$ . The *x*-ray patterns of the rarer minerals were not found in any available literature; in some cases, such patterns were nevertheless compared with those of chemical reagents. Samples of certain type specimens obtained from various museums were analyzed chemically. In some cases the material was originally identified on the basis of crude chemical, optical, or crystallographic determinations, and proved to be rather poorly characterized.

### DESCRIPTIONS OF SPECIMENS

#### *Mascagnite*

Artificial  $(\text{NH}_4)_2\text{SO}_4$  has  $N_x = 1.5209$ ,  $N_y = 1.5230$ ,  $N_z = 1.5394$ ;  $2V = (+) 52^\circ$ ;  $X = c$ ,  $Y = b$ ,  $Z = a$  (Winchell, 1931, p. 216). Reagent ammonium sulfate yields the *x*-ray data shown in Table 1, column 3 (A.S.T.M. Joint Committee on *X*-ray Data, 1950).

Mascagnite was not found with the fossil birds or eggs. The following museum materials are labelled mascagnite: (1) Brush Collection (Yale) No. 1693, mascagnite from Geysers, Sonoma [County, California], whose optical properties agree closely with those quoted above, gives the *x*-ray powder diffraction data recorded in Table 1, column 1. (2) Peabody Collection (Yale) No. 8971, mascagnite from Naples, Italy, whose optical properties also agree closely with those of reagent material, gives the *x*-ray powder data recorded in Table 1, column 2. (3) A Vaux Collection (Philadelphia Acad. Nat. Sci.) No. 15339, "mascagnite" from Etna, Italy, proved to be a mixture of sulfur and salammoniac. (4) Vaux Collection (Philadelphia Acad. Nat. Sci.) No. 5574, "mascagnite" from Chinch Islands is considered to be the material which Taylor (1859, p. 309) described as "? glaserite" and which Dana (1892, p. 895) called

taylorite and accepted as a new species. This material is treated under *taylorite*.

TABLE 1. X-RAY POWDER DATA FOR MASCAGNITE

1		2		3	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
5.44	1	5.16	2	5.2	2
4.96	9	4.27	10	4.36	10
4.65	3	3.87	5	3.91	2
4.31	4	3.08	8	3.12	4
3.74	8	3.00	8	3.03	4
3.36	10	2.62	1	2.67	0.7
3.04	1	2.495	1	2.51	0.7
2.90	7	2.298	4	2.32	2
2.68	1	2.161	4	2.18	2
2.475	3	1.937	1	2.05	0.1
2.321	1			1.97	0.4
2.196	2			1.93	0.2
1.884	1			1.77	0.2
				1.73	0.2
				1.70	0.2
				1.63	0.5
				1.56	0.2
				1.52	0.2
				1.49	0.5

1. Brush Collection (Yale) No. 1693 mascagnite, Sonoma County, California.

2. Peabody Museum (Yale) No. 8971 mascagnite, Naples, Italy.

3. A.S.T.M. card file, ammonium sulfate.

### *Arcanite*

Artificial  $K_2SO_4$  is orthorhombic with  $N_x=1.4935$ ,  $N_y=1.4947$ ,  $N_z=1.4973$ ;  $2V=(+)$   $67^\circ 20'$ ;  $X=b$ ,  $Y=a$ ,  $Z=c$  (Winchell, 1931, p. 217). Although this material has reportedly been found among guano materials, none was found in the specimens studied. An x-ray pattern of artificial  $K_2SO_4$  from the reagent shelf was made for reference purposes; its measurements agree satisfactorily with published data (A.S.T.M. Joint Committee on X-ray Data, 1950). The refractive indices of reagent  $K_2SO_4$  quoted above were confirmed within an experimental error of  $\pm .0010$ .

### *Taylorite and the arcanite-mascagnite series*

Dana proposed the name *taylorite* for material from the Chincha Islands described by Taylor (1859, p. 309) as “?glaserite.” Taylor ana-



lyzed the material and computed the formula  $(K, NH_4)_2SO_4$ . Taylor's analysis (Taylor, 1859, p. 309; Dana, 1892, p. 895; molecular proportions based upon modern atomic weights) follows:

			Formula
SO <sub>3</sub>	48.40%	.604 mol.	
(NH <sub>4</sub> ) <sub>2</sub> O	5.37	.127	K <sub>2</sub> NH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ; more exactly,
K <sub>2</sub> O	43.45	.491	K <sub>2-x</sub> (NH <sub>4</sub> ) <sub>x</sub> SO <sub>4</sub> , with x=0.42
Na <sub>2</sub> O	1.68		
	<hr/>		
	98.90		

Taylor described the specimens as occurring in "lumps or concretions about the size and shape of a hickory nut, of a white or creamy color." Some specimens in the Vaux Collection of the Philadelphia Academy of Natural Sciences (Vaux No. 5574), labelled "Mascagnite, Chincha Islands," fit this description perfectly. This material gives an x-ray powder pattern (Table 2, column 1) different from that of mascagnite (Table 1), but agreeing with those of two correctly labelled taylorite specimens from Guanapé. Its optical properties differ from those of mascagnite. No other specimens of guano materials in the Vaux Collection have this habit. The probability seems very good that the specimens, Vaux No. 5574, are actually the type material for taylorite. A new chemical analysis yielded the following results:

Taylorite: Vaux Collection, No. 5574, "Mascagnite, Chincha Is."

			Formula
SO <sub>3</sub>	45.18%, 45.55%	.570	
(NH <sub>4</sub> ) <sub>2</sub> O	5.14 ± .02	.099	K <sub>2-x</sub> (NH <sub>4</sub> ) <sub>x</sub> SO <sub>4</sub> , with x=about 0.35, depending upon assumptions as to the low summation.
K <sub>2</sub> O	47.50	.501	
Na <sub>2</sub> O	.0001	.600	
	<hr/>		
	97.87		

The SO<sub>4</sub> determination was by precipitation as the sulfate, done twice by Benoit; ammonia was determined by Nessler's colorimetric method by T. Sippel; K<sub>2</sub>O and Na<sub>2</sub>O were determined spectrographically by V. T. Bowen.

New determinations of the optical properties by Emmons' double-variation method (1929) gave the results shown in the second column of Table 3. A specimen labelled taylorite from Guanapé, Peru, obtained by Professor Hutchinson from the American Museum of Natural History, gave the data shown in the third column. Data of Larsen (1921, p. 142) are probably in error; although Larsen's data were obtained from a sample labelled taylorite, Frondel\* states that they were clearly obtained from some other mineral. The apparent discrepancy in optic

\* Frondel, C., Private communication, May 8, 1950; Frondel, 1950, p. 597.

TABLE 2. X-RAY POWDER DATA FOR TAYLORITE

1		2		3	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
4.21	8	4.19	8	4.20	7
3.77	1	3.79	2	3.77	1
3.40	2	3.39	1	3.42	2
3.04	7	3.03	9	3.04	9B
2.92	10	2.90	10	2.91	10
2.51	2	2.53	4	2.51	4
2.45	2	2.46	3	2.44	3
2.39	2	2.40	2	2.40	1
2.24	3B	2.23	3B	2.23	4
2.11	6	2.10	5	2.11	6
2.02	1	2.04	1	2.03	1
1.95	1	1.95	1	1.91	4
1.90	2	1.90	2	1.78	2
1.79	1	1.69	1B	1.69	3B
1.70	1	1.59	1	1.58	3
1.67	1	1.455	2	1.450	5
1.59	2	1.359	1B	1.394	1
1.453	2	1.308	1B	1.361	3
1.363	2			1.307	2
				1.256	2B
				1.226	1
				1.187	2
				1.156	2
				1.098	2
				1.054	2
				1.025	1

1. Vaux Collection (Phil. Acad. Nat. Sci.) No. 5574 labelled "Mascagnite Chincha Islands," probably type taylorite.

2. Vaux Collection No. 17879 taylorite Guanapé, Peru.

3. Amer. Mus. Nat. Hist. taylorite Guanapé, Peru, No. 16211.

sign and the variability of 2V are explained when it is noted that the material is apparently uniaxial at two compositions (near  $\text{Ar}_{50}\text{Ms}_{50}$  and  $\text{Ar}_{85}\text{Ms}_{15}$ ), and changes optic sign twice in the series. Note the orientations shown for the end members in Table 3, the crystal axis *c* becoming successively the vibration direction of X, of Y, and of Z, while *a* is the vibration direction of Z for most of the series, becoming Y when *Nc* exceeds *Na*; *b* is the vibration direction Y, becoming X when *Nc* exceeds *Nb*.

If a series be postulated between mascagnite and arcanite, the new optical data from Taylor's presumed type specimen from the Vaux Col-

lection fit the values interpolated from the end members of the series (Table 3).

TABLE 3. OPTICAL CONSTANTS OF THE ARCANITE-MASCAGNITE SERIES

Name Composition Locality	Arcanite $K_2SO_4$ Artificial <sup>1</sup>	Taylorite Ar+Ms		Mascagnite $(NH_4)_2SO_4$ Artificial <sup>1</sup>
		Chincha Is. <sup>2</sup>	Guanapé <sup>3</sup>	
$N_x$	$N_b=1.4935$	1.5008	1.5007	$N_e=1.5209$
$N_y$	$N_a=1.4947$	1.5037	1.5034	$N_b=1.5320$
$N_z$	$N_c=1.4973$	1.5062	1.5048	$N_e=1.5394$
2V	(+) 67°	lg	(-) sm., var.	(+) 52°

<sup>1</sup> Winchell, 1931.

<sup>2</sup> Vaux Collection No. 5574.

<sup>3</sup> Amer. Mus. Nat. Hist. No. 16211.

### *Aphthitalite*

Frondel (1950) states that the proper formula for aphthitalite is  $(K,Na)_3Na(SO_4)_2$ . Winchell (1933, p. 96) indicates that the material is uniaxial positive,  $N_o=1.487-1.491$ ,  $N_e=1.492-1.499$ . Bellanca (1943) worked out the crystal structure and determined the following physical data for material from Vesuvius:  $N_o=1.4882$ ,  $N_e=1.499$ , spec. gr. 2.697, axial ratio  $c/a=1.290$ . Frondel (1950) noted ammonian aphthitalite in guano from Guanapé.

Material from a fossil egg of *Pelecanoides garnoli* from Peruvian guano was analyzed by Mrs. Jane K. Setlow (Hutchinson, 1950, p. 94, anal. XI), with the result shown in Table 4, column 1. Optical and x-ray data for this specimen are given in Tables 4 and 5, as also for an aphthitalite from Searles Lake. The fossilized egg is an ammonian variety quite similar to that described by Frondel (1950), which is included in Table 4, column 2, for comparison. The Searles Lake aphthitalite (column 3) is without ammonia.

Druzinin (1938) investigated the system  $K_2SO_4-Na_2SO_4-H_2O$ , and reported that the compound  $K_3Na(SO_4)_2$  permits substitution of Na for K within the range  $K/Na=2.44$  to 3.00. Specific gravity and gonio-metric data are given for the solid solutions. If K and  $NH_4$  are written together the ratio of these to sodium according to analysis 1, Table 4 ( $46/17=2.71$ ), is within the limits given by Druzinin.  $NH_4$  and K have similar ionic radii (Goldschmidt, 1945) and should be expected to substitute for each other rather freely. The *P. garnoli* fossilized egg is therefore an ammonian aphthitalite similar to that found by Frondel in guano from Guanapé.

X-ray powder data for the materials from the fossil egg and for the Vesuvius and the Searles Lake specimens already cited with optical data are listed in Table 6. Aphthitalite from Vesuvius was analyzed by Bianchini (1937), but there is no reason to correlate his analysis with the physical properties reported here.

TABLE 4. CHEMISTRY AND OPTICS OF APHTHITALITE

	1		2	3	4
	Fossil egg, Peru <sup>1</sup>		Guanapé <sup>2</sup>	Searles Lake, Calif. <sup>3</sup>	Vesuvius <sup>5</sup>
(NH <sub>4</sub> ) <sub>2</sub> O	5.72%	.11 mol.	6.58		
K <sub>2</sub> O	32.88	.35	33.87	39.1	
Na <sub>2</sub> O	10.42	.17	9.65	8.0	
SO <sub>3</sub>	47.46	.60	48.62	43.6	
P <sub>2</sub> O <sub>5</sub>	1.33		0.70		
NaCl				7.9	
Oxalate (C <sub>2</sub> O <sub>3</sub> )	0.35				
Insol.	0.60				
H <sub>2</sub> O			0.21	0.1	
Sum	98.76		98.73	98.7	
N <sub>o</sub>	1.4998 ± .0004		1.498 ± .002	1.490 ± .003 <sup>4</sup>	1.498 ± .004
N <sub>e</sub>	1.5026 ± .0004		1.503 ± .002	1.496 ± .003	1.505 ± .004

<sup>1</sup> Aphthitalite. Fossil egg of *Pelecanoides garnoti* (Hutchinson, 1950, p. 94, anal. XI). Optics by H. Winchell. Analyst, Setlow.

<sup>2</sup> Ammonian aphthitalite, Guanapé (Fron del, 1950). Optics by Frondel. Analyst, Gonyer.

<sup>3</sup> Aphthitalite, Searles Lake, California. Recalculated from Foshag (1920).

<sup>4</sup> Brush No. 4436, Aphthitalite from Searles Lake, gives N<sub>o</sub> = 1.4905, N<sub>e</sub> = 1.4979, both ± .0004.

<sup>5</sup> Aphthitalite, Vesuvius. Vaux Collection No. 19480. Optics by H. Winchell.

### Lecontite

Taylor (1858) described a mineral from bat guano from a cave near Comayagua, Honduras, and on the basis of his analysis concluded it was a new species for which he proposed the name lecontite. Taylor's analysis is given below, with molecular proportions based on modern atomic weights:

(NH <sub>4</sub> ) <sub>2</sub> O	12.94%	.248 mol.	} .277
K <sub>2</sub> O	2.76	.029	
Na <sub>2</sub> O	17.56	.283	
SO <sub>3</sub>	44.97	.562	
H <sub>2</sub> O	19.45	1.080	
Organic residue	2.30		
Inorganic residues	.11		
Phosphoric acid	tr.		

100.09

TABLE 5. X-RAY POWDER DATA FOR APHTHITALITE

1		2		3	
<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>
4.04	7	4.98	4	4.98	3
3.66	4	4.11	6	4.10	6
2.92	8	3.66	5	3.69	5
2.81	10	2.94	8	2.97	9
2.42	1	2.82	10	2.85	10
2.32	2	2.46	5	2.46	6
2.02	9	2.31	3	2.34	4
1.81	1	2.24	1	2.19	×
1.63	3	2.18	1	2.09	9
1.52	1	2.05	9	1.852	1B
1.406	2	1.84	2	1.725	×
		1.74	1	1.656	3
		1.65	6B	1.603	×B
		1.60	1	1.544	1
		1.54	4	1.471	2
		1.469	3	1.425	3B
		1.423	5	1.310	×
		1.366	1	1.287	1
		1.331	1	1.266	×
		1.313	1	1.229	×B
		1.284	2		
		1.268	1		
		1.236	2		
		1.196	1B		
		1.169	1		
		1.155	1		
		1.123	1		
		1.098	1		
		1.079	2		

- 1. Aphthitalite, Vesuvius, Vaux No. 19480.
- 2. Egg of *Pelecanoides garnoti*, Am. Mus. Nat. Hist.
- 3. Aphthitalite, Searles Lake, Brush No. 4436.

Winchell (1933, p. 97) gives the formula  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , and the following optical properties:  $X=a$ ,  $Y=c$ ,  $Z=b$ ;  $N_x=1.440$ ,  $N_y=1.452$ ,  $N_z=1.453$ ;  $2V=(-) 43^\circ$  with dispersion  $r>v$ . A calculation based on modern atomic weights indicates a formula  $(\text{NH}_4,\text{K})\text{NaSO}_4 \cdot 2\text{H}_2\text{O}$  with  $\text{NH}_4/\text{K}$  about 8.5.

Using the law of Gladstone and Dale, and specific refractive energies furnished by Larsen (1934, p. 31), with the analytical and optical data now available it is possible to estimate the specific gravity of lecontite as about 2.5. This estimate differs from the known specific gravity (2.68) of thenardite by about 0.2, which is probably significant. Suitable material for a good determination apparently has never been studied. There are also differences in the x-ray powder patterns of lecontite and thenardite, as shown in Table 6.



Vaux Collection specimen No. 15337 Lecontite, Comayagua, Honduras, appears to be Taylor's type material for this species because the sample fits Taylor's physical description even including the bat hairs. The material is so fine grained that only an average index of refraction could be obtained.  $N_y = 1.495 \pm .010$ . Table 6 shows the x-ray data for this lecontite and for a similar specimen in the Brush Collection (Yale), No. 1696, received directly from Taylor, and also including the bat hairs. The pattern of reagent sodium sulfate (thenardite), in the same table is somewhat similar, but differs significantly from that of lecontite.

TABLE 6. X-RAY POWDER DATA FOR LECONTITE AND THENARDITE

1		2		3	
$d \text{ \AA}$	$I$	$d \text{ \AA}$	$I$	$d \text{ \AA}$	$I$
5.54	1	5.61	4	4.63	8
5.07	10	5.01	10	3.82	2
4.65	9	4.62	8	3.17	4
4.37	8	3.90	3B	3.07	4
3.87	6B	3.39	3B	2.78	10
3.43	1	3.04	9	2.64	8
3.30	1	2.86	1B	2.33	6
3.19	1	2.68	8	2.20	1
3.02	7	2.161	2	1.92	0.5
2.84	1	1.981	3	1.86	8
2.77	6	1.873	3	1.80	1
2.63	6			1.67	4
2.475	1			1.60	1
2.411	1			1.55	3
2.327	4			1.50	2
2.151	1			etc.	
2.049	1				
1.965	1				
1.855	5				
1.670	1				
1.605	1				
1.551	1				

1. Vaux Collection No. 15337 lecontite, Comayagua, Honduras

2. Brush Collection No. 1696 lecontite from cave of Las Piedras, Comayagua, Honduras, received from Taylor.

3. Thenardite. Reagent sodium sulfate.

The only other recorded lecontite is mentioned by Lacroix (1912) whose account is as follows (R. J. B., *Transl.*): "Embedded in the guano one finds nodules about the size of a walnut consisting of a water soluble salt, efflorescent in air. On ashing the material loses 59% of its weight;

this part consisting of water and  $(\text{NH}_4)_2\text{SO}_4$ ; the residue is essentially  $\text{K}_2\text{SO}_4$ . A necessarily summary analysis because of the small quantity available was done by M. Arsandaux and indicated a composition of approximately

45.7%	$\text{K}_2\text{SO}_4$
28.1%	$(\text{NH}_4)_2\text{SO}_4$
25.0%	$\text{H}_2\text{O}$

"The mineral is colorless, does not seem to possess a good cleavage, and is biaxial positive; the angle of the optic axes seems small [faible]. The only known substance which corresponds to this composition is lecontite  $\text{SO}_4(\text{NH}_4, \text{Na}, \text{K})_2 \cdot 2\text{H}_2\text{O}$  which occurs under similar conditions (in caves) at Las Piedras in Central America. The latter is optically negative. The mineral we are dealing with is probably an analogue rich in potassium."

#### *Oxammite*

" $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ." Orthorhombic  $2V = (-) 62^\circ$ ;  $N_x = 1.438$ ;  $N_y = 1.547$ ;  $N_z = 1.595$ ;  $X = c$ ,  $Y = a$ ,  $Z = b$  (Winchell, 1933, p. 89). From guano of the Guanapé Is., Peru.

Shepard (1870) described "oxalate of ammonia in very delicate but perfect crystals, which, as it has not been described as a natural substance, may receive the name oxammite." Shepard did not indicate that the material was a hydrate. (Cf. the section below on material from the mummified birds.)

Shepard (1870) described a material for which he proposed the name guanapite. His analysis of the material is given below:

Sulfate of potash	67.75%
Sulfate of ammonia	29.20%
Oxalate of ammonia	3.75%

In the same article he described a substance

Sulfate of potash	40.20%
Oxalate of ammonia	29.27%
Water	30.46%

and proposed the name guanoxalite. Whether or not the two substances are simply mixtures of substances like taylorite and oxammite could not, of course, be demonstrated unless Shepard's type material were available. There is no available evidence for their homogeneity. Whether true sulfoxalates exist has not, so far as we are aware, been determined; an investigation of the system  $(\text{NH}_4)\text{K}_2\text{SO}_4 - (\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  should settle the question of the existence of guanoxalite.

A fossil penguin egg from the Columbia University Collection was analyzed with the result shown in Table 7 (Hutchinson, 1950, p. 94,

anal. XII). The analysis indicates a formula  $(\text{NH}_4)_2\text{O} \cdot \text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , that is, a monohydrate. Optical study of the material yielded  $N_x = 1.440$ ;  $N_y = 1.470$ ;  $N_z = 1.580$  which agree with the published data for oxammite. Table 8 shows the x-ray data for fossil egg material, for material from Shepard's mummified birds, and for reagent ammonium oxalate monohydrate.

TABLE 7. CHEMISTRY OF OXAMMITE

			Deduct $\text{Na}_3\text{PO}_4$	Deduct Arcanite	Remainder Oxammite
$\text{SO}_3$	8.22%	.103 mol.		.103	
$(\text{NH}_4)_2\text{O}$	29.09	.562		.037	.525
$\text{K}_2\text{O}$	5.91	.066		.066	
$\text{Na}_2\text{O}$	5.87	.095	.087		(.088)
Oxalate (as $\text{C}_2\text{O}_3$ )	37.39	.519			.519
$\text{P}_2\text{O}_5$	4.14	.029	.029		
$\text{H}_2\text{O}$ (by diff.)	8.85	.491			.491
Insol.	0.53				

ANALYST, *Mrs. J. K. Setlow.*

TABLE 8. X-RAY POWDER DATA FOR OXAMMITE

1		2		3	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
6.33	7	6.37	10	6.46	8
3.79	6	3.83	7	3.83	7
3.23	4	3.45	x	3.49	x
3.05	5	3.28	6	3.29	6
2.88	5	3.08	7	3.07	6
2.67	10	2.88	8	2.88	6
2.60	10	2.68	8	2.68	10B
2.45	4	2.60	8	2.62	10B
2.39	4	2.47	6	2.47	6B
2.15	1	2.39	6	2.40	6B
		2.16	4	2.16	5
		2.07	3B	2.02	3
		2.02	3B	1.89	4B
		1.86	2B	1.84	4B
		1.76	2B	1.75	2
		1.69	1	1.69	1

1. Oxammite from fossil egg of a penguin (*Spheniscus humboldti*) from the Roebling collection of Columbia University (Hutchinson, 1950, p. 94).
2. Oxammite from Shepard's mummified birds, Peabody Museum (Yale).
3. Reagent  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .

An analysis by Tanner, quoted by Dana (1892, p. 994) gives the composition of an ammonium oxalate from Guanapé, Peru, which is very close to  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , and which appears to be the only analysis of the material, and the only evidence that a dihydrate exists as a natural substance.

Professor J. H. Yoe of the University of Virginia, where Tanner's original type specimen should be located, stated\* that the material was probably lost in a fire which destroyed the chemistry laboratory in 1916.

By a fortunate coincidence the Peabody Museum at Yale contains some mummified birds which were from the boatload of guano that Shepard examined. This material is thus as close an approach to type oxammite as now can be obtained. Four specimens of crystalline material were picked off the skin of these sub-fossils and all four had diffraction patterns (Table 8, col. 2) identical with that of reagent ammonium oxalate monohydrate.

The ordinary laboratory salt is the monohydrate. Winchell (1943, p. 25) gives the indices in Na light for artificial monohydrate as  $N_x = 1.4383$ ;  $N_y = 1.5475$ ;  $N_z = 1.5950$ ;  $2V = (-) 61^\circ 44'$ ;  $X = c$ ;  $Y = a$ ;  $Z = b$ .

The analysis of the material from the fossil egg agrees with  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . This material and material from Shepard's mummified birds agree with reagent monohydrate in x-ray diffraction pattern and indices of refraction. Evidently Shepard had a monohydrate and the name oxammite should be reserved for naturally occurring ammonium oxalate monohydrate.

#### SUMMARY

Taylorite is essentially ammonian arcanite. It has been found in guano of both the Chincha and Guanapé Islands. Taylor's original type specimen is believed to be in the Vaux Collection, and labelled mascagnite. A small sample from this specimen has been analyzed, establishing the mineral as an ammonian arcanite. Ammonian apththitalite occurs as a guano mineral in Peru. Oxammite from the same cargo as Shepard's type material gives an x-ray diffraction pattern identical with that of ammonium oxalate monohydrate, which was also found replacing a penguin egg. X-ray and optical data are given for these minerals. Lecontite appears to be a valid species.

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# A RESTUDY OF THE SOCIAL CIRCLE, GEORGIA, METEORITE

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AND

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## ABSTRACT

A new analysis and density determination are reported for the Social Circle meteorite. This iron is evenly granulated throughout; this is believed to be due to reheating after the octahedral pattern formed, but before the meteorite entered our atmosphere.

This meteorite was found while plowing a field on the plantation of W. B. Spearman, near Social Circle, Walton County, Georgia, in 1926. The meteorite weighed 219 pounds and the length, breadth and thickness of it was given by S. W. McCallie<sup>2</sup> as fifteen, thirteen and nine inches, respectively, in the only published data on this meteorite.

This iron is believed to be an old fall because the outer surface is so weathered that no remnants of the original crust remained. Flight markings as well as the fusion crust, under average conditions, usually persist for a number of years. The surface of this meteorite, however, was so weathered that any shallow depressions or thumb marks which may have been present were completely obliterated. Hence the Social Circle iron must have fallen many years before it was found.

Shortly after the main mass was cut in the laboratories of the U. S. National Museum it was found to contain lawrencite, hence the alteration may have been somewhat accelerated by this agent. In places the weathering had penetrated about one centimeter below the present outside surface of the specimen.

When the preliminary investigation on this iron was made, probably for the purpose of identifying it as a meteorite, an unsightly notch was cut into the thin edge of the mass. This notch was about three inches deep, and as the two saw cuts did not meet there has been some speculation as to how the wedge-shaped piece of metal was removed.

Then, since the original analysis of this iron appeared to be inconsistent with the width of the granulated kamacite bands, and some speculation arose about the granulation extending evenly through the entire meteorite, these authors made an effort to obtain the main mass for restudy. Through the cooperation of Captain Garland Peyton, Director, and Dr. A. S. Furcron, Assistant Director, of the Georgia Department

<sup>1</sup> Published by permission of the Secretary of the Smithsonian Institution.

<sup>2</sup> Notes of Social Circle Meteorite, *Am. Jour. Sci.*, 5th ser., **13**, 360 (1927).

of Mines, Mining and Geology, the Social Circle meteorite was sent to the U. S. National Museum with permission to section it.

A new cut was made parallel to the long dimension of the meteorite and far enough into the specimen to remove the unsightly notch. Thus a large cross section was prepared and from this sizable mass a number of slices were cut at right angles to the large cross section.

The largest cross section through this iron measures seventeen by eight and one half inches and has approximately one hundred square inches of surface. This was polished and etched, as were all of the eight sections which were cut at right angles to the larger cross section. After examining all of these surfaces it was apparent that the entire meteorite has the same degree of granulation. This is believed to be a significant point.

TABLE 1. COMPOSITION OF THE SOCIAL CIRCLE, GEORGIA, METEORITE

	1	2	
Fe	94.07	91.83	
Ni	5.02	7.44	
Co	.38	.38	
Cu	trace	—	
Sn	.09	—	
P	.06	trace	
	99.62	99.65	Mol. Rat.
			$\frac{\text{Fe}}{\text{Ni} + \text{Co}} = 12.43$
Specific Gravity	7.42	7.81	
Specific Gravity		7.89	

1. Edgar Everhart analyst, *op. cit.*

2. E. P. Henderson, analyst.

The difference in specific gravities may be due to the fact that the original determination was made upon a piece of metal which was slightly oxidized.

This iron although granulated still shows outlines of the octahedral structure. The kamacite bands average between .3 and .5 millimeter in width, hence the Social Circle iron is a fine octahedrite. The kamacite bands are separated by long narrow taenite lamellae, but the kamacite is uniformly granulated. No appreciable difference in the degree of granulation was noted in any of the sections. Although the long taenite lamellae were not broken up, the plessite areas have been modified and their structure transformed to a granular texture.

Only a few inclusions of schreibersite and troilite were noted. The temperature required to produce any effect on either of these constituents

is far above that which is necessary to granulate kamacite. To alter plessite would require still greater heating, because it takes higher temperatures to alter taenite bodies than it does either to diffuse phosphide or to granulate kamacite.



FIG. 1. Cross section of the Social Circle Meteorite showing that it is evenly granulated throughout. Weathering had removed all the original external features from this iron and the dark areas around the edge show the distance weathering had penetrated. This meteorite contains some lawrencite.  $\frac{1}{4}$  natural size.

Farrington<sup>3</sup> published pictures of the Toluca iron showing its structure before and after heating to a temperature of 900° C for seven hours. The octahedral structure was all but completely destroyed. The temperature to which the Social Circle iron was reheated cannot be estimated because a prolonged heating at lower temperature, 600–700° C would probably be sufficient to produce the effect noted in this iron. Most likely it was gradually heated and the temperature to which it was raised must have been maintained long enough to heat it uniformly throughout. The degree and the duration of the heating of this iron were not enough to materially affect the taenite lamellae but were sufficient to alter the plessite fields.<sup>4</sup> The exact nature of that alteration is not clear to the authors. The appearance of the fields differs from that of similar fields of normal character. They present a darkened and confused pattern, the character of which is not clear even under high magnification. Conceivably minute particles of taenite in such a field might be affected by heating to a range that would not visibly affect lamellae of taenite. Or the field may

<sup>3</sup> Meteorites, p. 99, 1915. Published privately by the author.

<sup>4</sup> Perry, S. H., Metallography of Meteoric Iron: *U. S. Nat. Mus., Bull.* **134**, pl. 74 (1944).

have contained a dark gamma-alpha aggregate, common in such fields, which underwent alteration, but the original presence of which cannot now be affirmed.

Kamacite would be the first constituent to be affected by the heat because the solubility of the nickel in kamacite is reported to be gradually decreased as the temperature is raised above 400° C.<sup>5</sup> Kamacite at about 600° C will contain about 4 per cent of nickel and at 700° C the solubility of nickel is further reduced to about 2 per cent. Granulation could

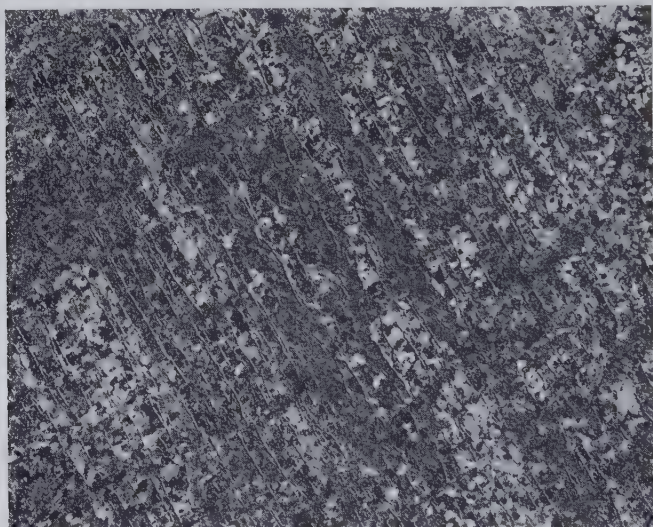


FIG. 2. The kamacite has been granulated by the reheating but the narrow taenite lines have not been affected. 5×

be attained, according to Tammann<sup>6</sup> by prolonged heating even at 400° C, but it would probably be a fine grained secondary granulation. It is estimated that the grain size of the kamacite in Social Circle meteorite was formed by heating to a much higher temperature. It is doubtful if a temperature of even 600–700° C would be high enough to alter the plessite fields unless it was sustained for a long time.

Many of the new boundaries of the granulated kamacite structure stop at taenite lamellae, and if they all did it certainly would be strong evidence that granulation was produced subsequent to the formation of the octahedral structure.

It is doubtful if granulation could be produced at temperatures of 400° C or less by even long and continued heating. At these low tempera-

<sup>5</sup> Owens and Sully: *Philos. Mag. Jour. of Science*, 27, no. 184, p. 614 (1939).

<sup>6</sup> Gustav Tammann: *Lehrbuch der Metallographie* (1923).



tures it would require an unusual set of conditions which are difficult to reconcile with the supposed formation of meteoritic structures. The heat would have to be maintained for an extremely long time because any rearrangement in the iron at these low temperatures would be very sluggish. Therefore these authors feel justified in stating that the granulation or reheating of the Social Circle iron was in no way related to its flight through our atmosphere.

Meteorites are only in the earth's atmosphere for a short time, measured in seconds, hence there is not enough time for the heat generated during the fall to penetrate very far into the mass. Evidence can be found in a limited number of polished sections of meteorites that the heat which develops during their flight penetrates the mass in localized areas. Rarely will the structures be modified as far as one centimeter below the outer surface.

The granulation in the Social Circle meteorite is not the result of man's attempt to apply heat. A number of the meteorites discovered a long time ago were heated in the blacksmith's forge. Such heating would not produce an even temperature throughout, because the surface would be heated to a higher degree than the interior, hence, the granulation near the outside would be different from that in the center of the iron. The Social Circle iron certainly was never heated under controlled conditions such as would be possible in a laboratory.

Because the time needed to uniformly heat this meteorite to the temperature required to produce the granulation observed, these authors believe that it was reheated, after it originally cooled, and after the octahedral pattern formed. The present concept most generally favored is that iron meteorites represent the internal core of a planet. Thus the reheating or granulation may have taken place while this meteorite was a part of the core of some planet-like body.

If this is the case, the gradual rise in temperature was connected with some internal heating in the planetary mass. However, the evidence gained from this examination of the Social Circle iron suggests that it was not reheated at the time the planet disrupted, because the temperature necessary for this degree of granulation was not high enough to have an intimate relationship with that catastrophic event.

The other explanation for the reheating of this meteorite is that it occurred after the planet had broken up and before it fell through our atmosphere to this earth. The next logical possibility to consider is that the mass strayed in close enough to our sun and remained there long enough to be heated throughout to the necessary temperature.

However, most astronomers seem to have rejected this possibility and feel that meteorites belong to our system and that they have elliptical



orbits like asteroids. Dr. Charles P. Olivier<sup>7</sup> has informed these authors "that some asteroids have orbits that take them inside of the orbits of Venus and one or two inside that of Mercury. Hence innumerable meteorites inevitably have the same orbits. Therefore, it is possible that this mass did have an elliptical orbit with a perihelion distance near enough to the sun to become heated. This meteor may have made several revisits near the sun before it finally crossed the earth's orbit at a time when we were in position to catch it."

Thus if its orbit could have taken it inside of Mercury it is most likely that the mass would have been heated long enough to produce the alteration in structure found in this meteorite.

The answer to the question as to where and how this meteorite was reheated is an astronomical problem and this point is being left to the astronomers.

The Social Circle iron when found weighed 219 pounds and no estimate is made of the amount of material that was lost through weathering. It must have been much larger before it entered our atmosphere because a great reduction in weight and considerable reduction in size occurs as a meteor passes through our atmosphere.

Since the original dimensions of the mass must have been greater than they are today, perhaps the original external portions were more granulated by reheating than the central core, but this material has been removed in the flight of the mass through our atmosphere. However, it seems reasonable to assume that an iron mass of several tons could be as uniformly heated, by the process mentioned above, as a smaller body.

#### ACKNOWLEDGMENTS

We wish to thank Doctors Carl A. Bauer, Charles P. Olivier and Harrison Brown for their suggestions in this investigation.

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<sup>7</sup> Private communications.

## ILSEMANNITE AND JORDISITE

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### ABSTRACT

Ilsemannite, a molybdenum mineral of uncertain composition, was identified in Oregon for the first time by the writer in 1939, in an ore specimen from the Kiggins mine on the Oak Fork of the Clackamas River. The occurrence is different from any previously described in that the ilsemannite is associated with cinnabar, the latter being of good enough grade to permit profitable mining during periods of high prices.

The ilsemannite occurs as a coating and alteration product of a fine-grained, black, sectile, submetallic material. Chemical and x-ray analyses of the original black material prove it to be an amorphous molybdenum disulfide. It is recommended that the name "jordisite," suggested by Cornu in 1909, be used for this material. Höfer and other writers have assumed ilsemannite was derived from wulfenite, other molybdates, or molybdenite.

Jordisite, possibly because of its amorphous state, alters more readily to ilsemannite than does molybdenite. This, together with the relative scarcity of jordisite in mineral deposits, probably accounts for the few known occurrences of ilsemannite in molybdenum districts.

### INTRODUCTION

The Kiggins mine on the Oak Fork of the Clackamas River, located about 50 miles southeast of Portland, Oregon, has been a small intermittent producer of quicksilver. In 1939, when the writer was engaged as geologist in charge of developing this property, he had an opportunity to collect several interesting suites of minerals from the mine. One of the gangue minerals associated with the cinnabar was identified as ilsemannite. Laboratory work later confirmed this field identification. A further study of the ilsemannite showed that it occurred as a coating on a black sectile material from which it was obviously derived. As the origin of ilsemannite has never been satisfactorily explained, a study of this material was undertaken in the hope of obtaining further information leading toward the solution of the problem.

### ACKNOWLEDGMENTS

Data for this paper were obtained in part from the chemical analyses made by Mr. K. C. Peer of San Francisco, and Mr. H. C. Frye of the Department of Chemistry, University of Oregon, and from the x-ray diffraction photographs obtained under the direction of Dr. J. D. H. Donnay of The Johns Hopkins University and Mr. A. J. Kaufmann, Jr., of the U. S. Bureau of Mines, Albany, Oregon. Two spectrographic analyses were made by Mr. T. C. Matthews of the Oregon State Department of Geology and Mineral Industries. The writer also wishes to acknowledge financial assistance from the Graduate School of the

University of Oregon which helped defray the expense of some of the analyses.

#### ILSEMANNITE

Andesites, probably of Miocene age, form the country rock in the region of the Kiggins mine. They are highly fractured, the most prominent trend of fractures being N. 45° W. Veins filling these fractures and related fissures contain cinnabar in commercial amounts. Calcite, pyrite, and stilbite are the principal gangue minerals.

The ilsemannite is found as veinlets and irregular lenses or pods closely associated with the cinnabar. Although ilsemannite is found in small amounts in many places in the mine, the richest occurrence is in the main tunnel (adit #1), 45 to 60 feet from the portal. Here the ilsemannite is in a calcite vein which varies in dip from 60° N. E. to almost vertical, and extends in a N. 45° W. direction along the adit. An underhand stope 6 feet deep, was put down on the calcite vein at this point and showed a concentration of both cinnabar and ilsemannite on the footwall.

Stilbite frequently occurs as a fissure filling with well-developed comb structure, the subhedral crystals often exceeding 5 cm. in length. In addition, fine-grained stilbite is intimately mixed with cinnabar, in the calcite veins. This close association of stilbite and cinnabar, although not common in quicksilver mines, is not anomalous since both minerals are characteristic of low temperature, epithermal deposits. The ilsemannite when first found has a dark blue-black color and often stains the calcite light blue. On exposure to sunlight the ilsemannite turns blue-green and fades. Some of the mineral was furnaceed along with the cinnabar and the calcined product emerged a purplish pink in color. Ilsemannite is soluble in water, first producing a greenish blue solution which later deepens to a typical molybdenum blue.

Although ilsemannite is not a common mineral, there are several known occurrences of it. It was first described by Höfer (1871) from Bleiberg, Carinthia. Since then it has been described from more than a dozen localities, but in spite of this there is still uncertainty regarding its origin and chemical composition.

Hess (1925, p. 9) has shown that Höfer in his original discussion of ilsemannite confused two substances, one a black material and the other a blue substance derived from the first. Hess remarks, "The black mineral that forms with water first a greenish-blue and then a blue solution may be a different mineral having perhaps some such relation to ilsemannite as anhydrite ( $\text{CaSO}_4$ ) has to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )."

Strunz (1941) describes ilsemannite as amorphous, and corresponding to the so-called blue molybdenum oxide. Dana (1944, pp. 602-603) well summarizes the situation by stating, "Possibly several different substances are repre-

sented among the natural occurrences." In general, most mineralogists seem to have applied the name "ilsemannite" to any molybdenum compound or mixture which is water soluble and turns the solution a typical molybdenum-blue color.

No method was worked out whereby the very thin coating of ilsemannite, often existing only as a stain on other water soluble minerals like halotrichite, could be separated from them. Consequently chemical analyses of this material were not obtained.

Underneath the coating of soluble sulfates and ilsemannite there was discovered a black, submetallic, sectile mineral which was first thought to be metacinnabar. Microchemical tests, however, proved it to be a molybdenum compound rather than a mercury mineral. It is obvious that the ilsemannite is derived from this black mineral, since the ilsemannite occurs as bluish spots, coatings, or along cracks where there was opportunity for ready alteration.

Ilsemannite is usually considered to be a secondary mineral and there has been considerable uncertainty concerning the primary or earlier mineral from which it was derived. Höfer (1871) believed the Bleiberg ilsemannite to be derived from wulfenite, as no other molybdates were known from the locality, but he had no positive evidence and based his conclusions on the fact that a molybdenum-blue coloration may be obtained by the action of concentrated sulfuric acid on wulfenite. Cook (1922), in studying ilsemannite from Shasta County, California, suggested molybdenite as the source mineral. Likewise, Lindgren and Ransome (1906, p. 124) believed that ilsemannite from Cripple Creek, Colorado, was a direct product of the oxidation of molybdenite. Hess (1925, p. 16) concluded that, "Ilsemannite, like wulfenite, is probably formed from some unknown mineral, perhaps a sulfide." The fact that molybdenite deposits so seldom are accompanied by ilsemannite makes it doubtful that molybdenite is usually the source of ilsemannite.

A study of the black mineral in polished sections and in fragments indicates that it is not molybdenite. It lacks cleavage, is dull black except where scratched, and then it has a submetallic gray black to lead gray appearance. It is soluble in concentrated  $\text{HNO}_3$ , very slightly soluble in  $\text{HCl}$  and insoluble in  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ . In the Clackamas occurrence it was deposited about the same time as the cinnabar and later than the calcite and stilbite. Figure 1 shows veinlets of the black mineral following the rhombohedral outlines of the calcite.

#### CHEMICAL DATA

Because the Clackamas material is an intimate mixture of molybdenum minerals with quartz, cinnabar, stilbite, pyrite, opal, halotrichite, and

calcite, separation for analysis is very difficult. Purification of the black mineral was accomplished first by removing the water-soluble minerals and then discarding all the other remaining minerals by hand-picking under the microscope. Two spectrographic analyses were made on this material, the first<sup>1</sup> showing Si and Ca greater than 10%; Al, Fe, Mo, ranging from 10% to 1%; Mg, As from 1% to 0.1%; Na, K, Mn, Ti, Ba, Sr, from 0.1% to 0.01%, and Cr, V, Cu, Bi, B, less than 0.01%. A second

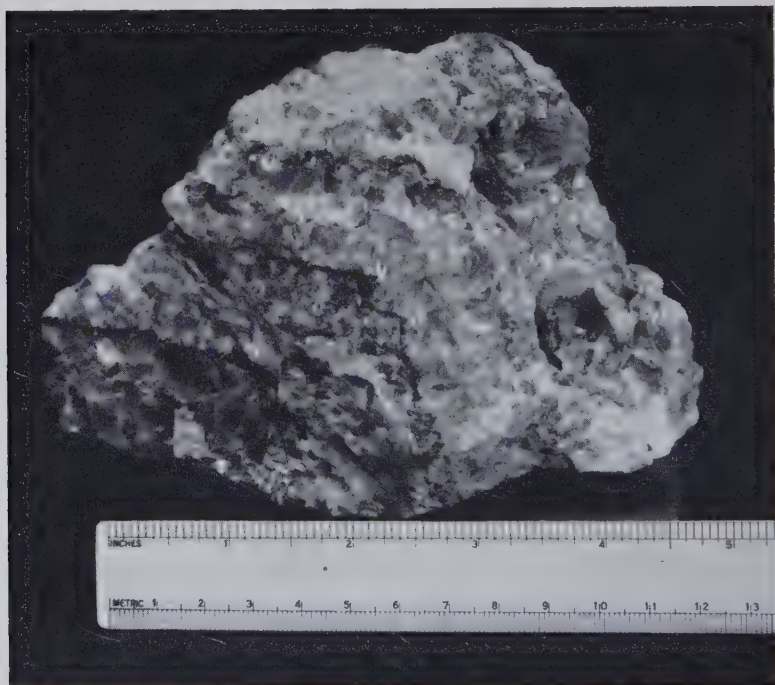


FIG. 1. Jordisite veinlets (black) with rhombohedral pattern outlining calcite.

spectrographic analysis on slightly purer material<sup>2</sup> obtained Si as the major constituent; Mo from 20% to 10%; Fe from 6% to 3%; Al from 0.5% to 0.1%; and smaller amounts of Ca, Na, Ba, Cu, Mn, Ni, Sr, Ti, and V. The question raised by these analyses was whether the black mineral was a complex salt such as a silicomolybdate of iron or aluminum, or whether most of the reported elements were due to impurities that were not removed.

<sup>1</sup> Analysis by Oregon State Department of Geology and Mineral Resources, T. C. Matthews, analyst.

<sup>2</sup> Analysis by Multiphase Laboratories, San Francisco, K. C. Peer, analyst.



Two small samples of the purified material were analyzed<sup>3</sup> and the following was determined to be the composition of the material:

Silica ( $\text{SiO}_2$ )	57.0
Molybdenum sulfide ( $\text{MoS}_2$ )	20.5
Iron sulfide ( $\text{FeS}_2$ )	9.3
Alumina ( $\text{Al}_2\text{O}_3$ )	1.2
Calcium compound ( $\text{CaX}$ )	0.6
Heavy metal sulfides (as $\text{HgS}$ ) also undetermined and traces	1.2
Total water	10.2
	<hr/> 100.0%

It was evident that the analyzed sample contained impurities of pyrite, stilbite, and cinnabar, so the presence of iron sulfide, alumina, calcium, and heavy metal sulfides was to be expected in the above analysis. The analysis indicated only a trace of sulfate sulfur, practically all of the sulfur appearing as sulfide sulfur. On distributing the sulfur between the iron and molybdenum, there was almost exactly the correct amount to yield the formula  $\text{MoS}_2$ , making it evident that although the material did not have the properties of molybdenite it was a molybdenum disulfide.

It was found possible to make a satisfactory bromoform separation of the material, thereby removing almost all of the cinnabar, pyrite, and calcite. As a further check for the presence of molybdenum disulfide an analysis<sup>4</sup> was made of some material purified in this manner. This showed only a trace of iron and when all the sulfide was applied to the molybdenum present it gave a ratio of 59.8% molybdenum to 40.2% sulfur, as compared with an ideal ratio of 60.0% to 40.0% for  $\text{MoS}_2$ , leaving no doubt that the compound is molybdenum disulfide.

#### X-RAY ANALYSIS

X-ray diffraction patterns were made on the material by Dr. J. D. H. Donnay and Mr. A. F. Rekus of The Johns Hopkins University. These exposures indicated the presence of considerable quartz which yielded the predominant pattern, and corroborated the chemical analysis. No additional match could be made from the weaker lines and a comparison with molybdenite from Haddam, Conn., and Ogden Mine, N. J., indicated that the black mineral was not molybdenite. Dr. Donnay<sup>5</sup> made the interesting observation that colloidal matter might be present as indicated by several broad bands in some of the films. These

<sup>3</sup> Analysis by Multiphase Laboratories, San Francisco, K. C. Peer, analyst.

<sup>4</sup> H. C. Frye, Dept. of Chem., Univ. of Oregon, analyst.

<sup>5</sup> Personal communication.

results were confirmed by x-rays<sup>6</sup> on material further purified by bromoform separation and the only pattern obtainable was that of quartz, with no evidence of the presence of any molybdenite. From these analyses it is concluded that the black mineral is an amorphous molybdenum disulfide.

### JORDISITE

Cornu (1909) stated that ilsemaninite is derived from a black powdery colloidal molybdenum sulfide which he called "jordisite." He gave no proof of this derivation nor did he describe jordisite. Hess (1925, p. 16) in commenting on this reference stated, "It does not convince one that his material was really a sulphide of molybdenum." So far as known no one has confirmed the occurrence of jordisite since Cornu's brief description. The present study on material from the Clackamas locality indicates that Cornu was correct in his statement that ilsemaninite is derived from a black colloidal molybdenum sulfide, and although Cornu did nothing to establish the name "jordisite," the occurrence in Oregon should confirm the name as a valid one for the mineraloid. Furthermore, unlike the most common occurrence of molybdenite, jordisite appears to be a low temperature product as indicated by its association with cinnabar and zeolites. This, together with the relative rarity of jordisite, may explain the scarcity of ilsemaninite in most molybdenite deposits. In those few cases where ilsemaninite has been reported as associated with or derived from molybdenite, it is likely that some jordisite was also present.

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*Manuscript received Oct. 4, 1950*

<sup>6</sup> Diffraction pattern by U. S. Bureau of Mines, Albany, Oregon.

# THE DIFFERENTIAL THERMAL ANALYZER AS A MICRO-CALORIMETER\*

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## ABSTRACT

Calorimetric measurements of very small magnitude are made possible by a sensitive method of differential thermal analysis. The increased sensitivity of the technique is due to the use of a low-mass radiation-type furnace operated in a vacuum, and at high heating rates. Calibration of the instrument was accomplished by employing the well-known reaction of calcite dissociation as a standard.

## INTRODUCTION

The technique of differential thermal analysis has been largely confined to the investigation of qualitative thermal characteristics of various mineral species. In particular, the clay minerals have been widely studied, and thermal analyses for these minerals are familiar to mineralogists, ceramists, and soil scientists.

Hitherto, the differential thermal analyzer has not been developed into a precise calorimetric tool. This paper describes a successful calibration of a differential thermal analyzer, so that it is able not only to detect, but also to measure heat changes as small as ten millicalories in magnitude. This device might well be termed a micro-calorimeter, and, as such, should be of interest to all physical scientists.

## APPARATUS

The apparatus used in this investigation was essentially the same as that described by Whitehead and Breger.<sup>1</sup> The controller and recorder were unchanged, but the mass of the entire furnace housing was reduced so that its design is that shown in Fig. 1. As a result of these changes, the furnace was brought under closer temperature control, especially at high heating rates, and thermal changes, as recorded by the thermographic curves, became highly magnified.

## THEORY OF METHOD

Cohn,<sup>2</sup> Macgee,<sup>3</sup> and Shorter<sup>4</sup> have described calibrations of differential thermal analyzers for use on ceramic bodies. All of these calibrations,

\* An investigation as part of a Ph.D. thesis by the author.

<sup>1</sup> Whitehead, W. L., and Breger, I. A., Vacuum differential thermal analysis: *Sci.*, **111**, 279-281 (1950).

<sup>2</sup> Cohn, W. H., The problem of heat economy in the ceramic industry: *J. Am. Cer. Soc.*, **7**, 475-488 (1924).

<sup>3</sup> Macgee, A. E., The heat required to fire ceramic bodies: *J. Am. Cer. Soc.*, **9**, 206-247 (1926).

<sup>4</sup> Shorter, A. J., The measurement of heat required in firing clays: *Trans. Brit. Cer. Soc.*, **47**, 1-22 (1948).

however, are on a macro scale, and entail a comparatively long and cumbersome procedure.

The method of calibration described here is simple. Briefly, it involved heating carefully weighed samples of a known reactive substance at a

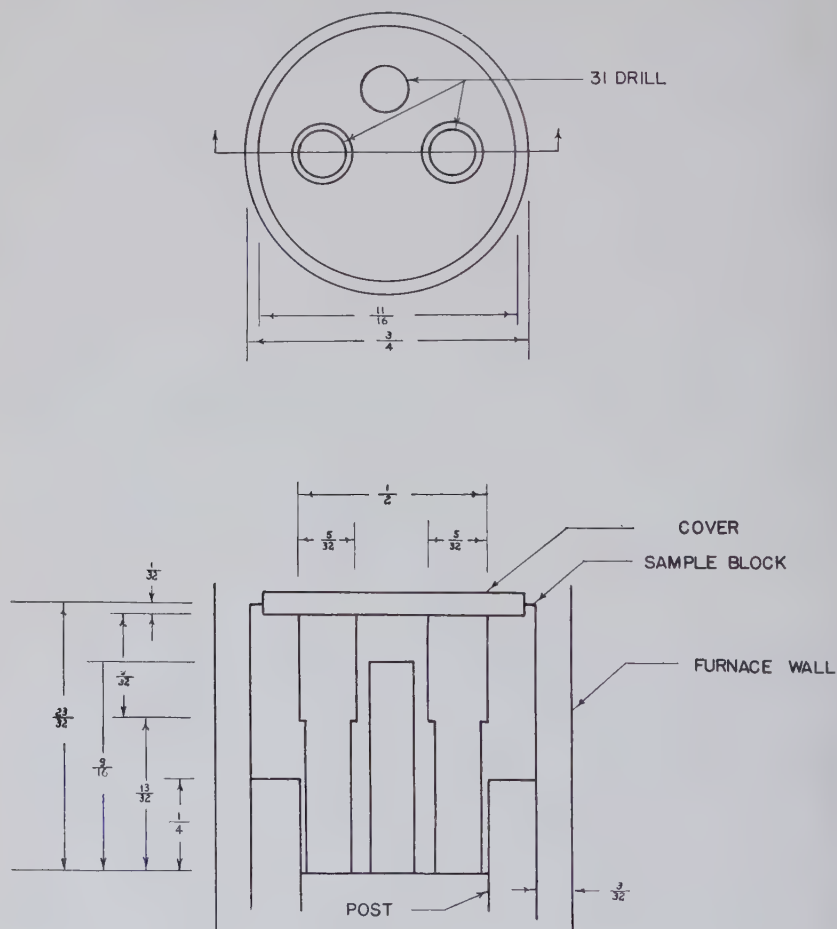


FIG. 1

constant rate, through its reaction temperature range, and then relating the energy changes with the corresponding responses (areas) recorded by the thermographic curves.

The theoretical basis upon which this calibration was developed, was formulated by Speil<sup>5</sup> and is briefly reviewed here with the aid of Fig. 2,

<sup>5</sup> Speil, S., Applications of thermal analysis to clays and aluminous materials: *U. S. Dept. of Int.—Bur. of Mines, R.I. 3764* (1944).

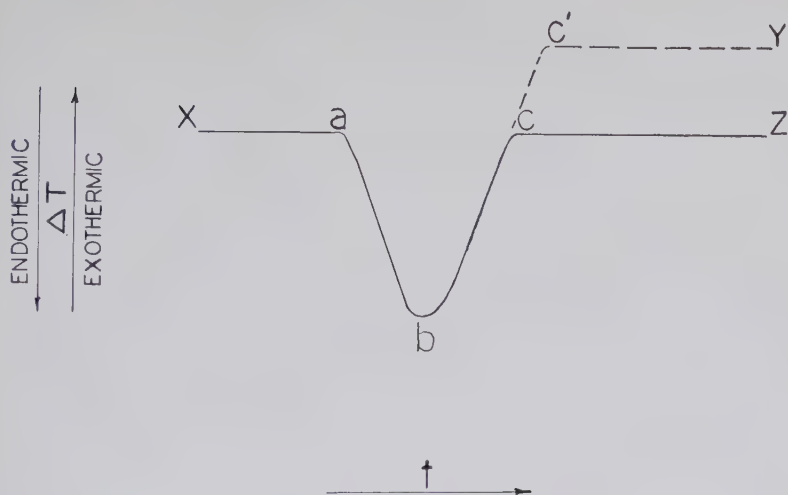


FIG. 2

a sample thermographic curve showing a reaction beginning at point *a*, and continuing towards point *c*.

$$(\text{Area}) abc \propto \int_a^c \Delta T dt = \frac{M(\Delta H)}{gk} \quad (1)$$

where,

*M* = mass of the reacting specimen

$\Delta H$  = specific heat of reaction

*g* = geometrical shape constant

*k* = thermal conductivity of the reacting specimen.

Equation (1) neglects the temperature gradient in the sample as well as some insignificant differential terms, and therefore is a close approximation. Transposing terms we get

$$(\text{Area}) abc \propto gk \int_a^c \Delta T dt = M\Delta H = Q \quad (2)$$

or,

$$(\text{Area}) abc \propto Q \quad (3)$$

where

*Q* = heat of reaction.

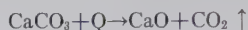
As an approximation, then, the area is a linear function of the heat of reaction as expressed by equation (3).

#### CALIBRATION

The reactive substance chosen for the calibration was  $\text{CaCO}_2$  (calcite)



which follows the reaction



beginning at a temperature of about 630° C. when heated statically. The values<sup>6</sup> for  $Q$  in the above reaction are very large and permitted samples smaller than the thermocouple head to be used. Later, the significance of these minute samples will be shown.

The dissociation of the  $\text{CaCO}_3$  samples at a heating rate of 30° C per minute in an evacuated furnace produced the thermographic curves shown in Fig. 3, and the relation between the area and the heat of reaction, as described above, gave the linear plot of the same figure. The validity of equation (3) is demonstrated by the experimental evidence displayed by the linear plot. Table 1 is a summation of the experimental and calculated data of the calibration.

TABLE 1

Sample	Reactive Sample		Thermographic Response (Area in Sq. In.)
	Weight (milligrams)	Heat of Reaction (millicals.)	
A	0.30	123	0.294
B	0.40	165	0.363
C	1.00	410	0.900
D	1.50	614	1.385
E	2.10	853	1.910
F	2.50	1015	2.283
G	3.00	1215	2.721

Measurements of areas were made with a planimeter and checked by means of a simple grid. The measurement of the areas, however, was the crux of the entire calibration since the area is not always clearly defined. In Fig. 2 the thermographic base-line X-Z is not linear in the general case. It is obvious that when a large sample is tested in the differential thermal analyzer, a major reaction is usually accompanied by a sharp change in the thermal conductivity and the specific heat capacity of the specimen. This results in a thermal gradient between the differential thermocouples that gives rise to a non-linear base-line. In Fig. 2 point  $c$  is often displaced towards  $c'$ , and the curve continues toward Y. In addition, slow heating rates (12° C. per minute) decrease the slope of  $ab$

<sup>6</sup> Smyth, F. H., and Adams, L. H., The system, calcium oxide-carbon dioxide: *Jour. Am. Chem. Soc.*, **45**, 1167-1184 (1923).

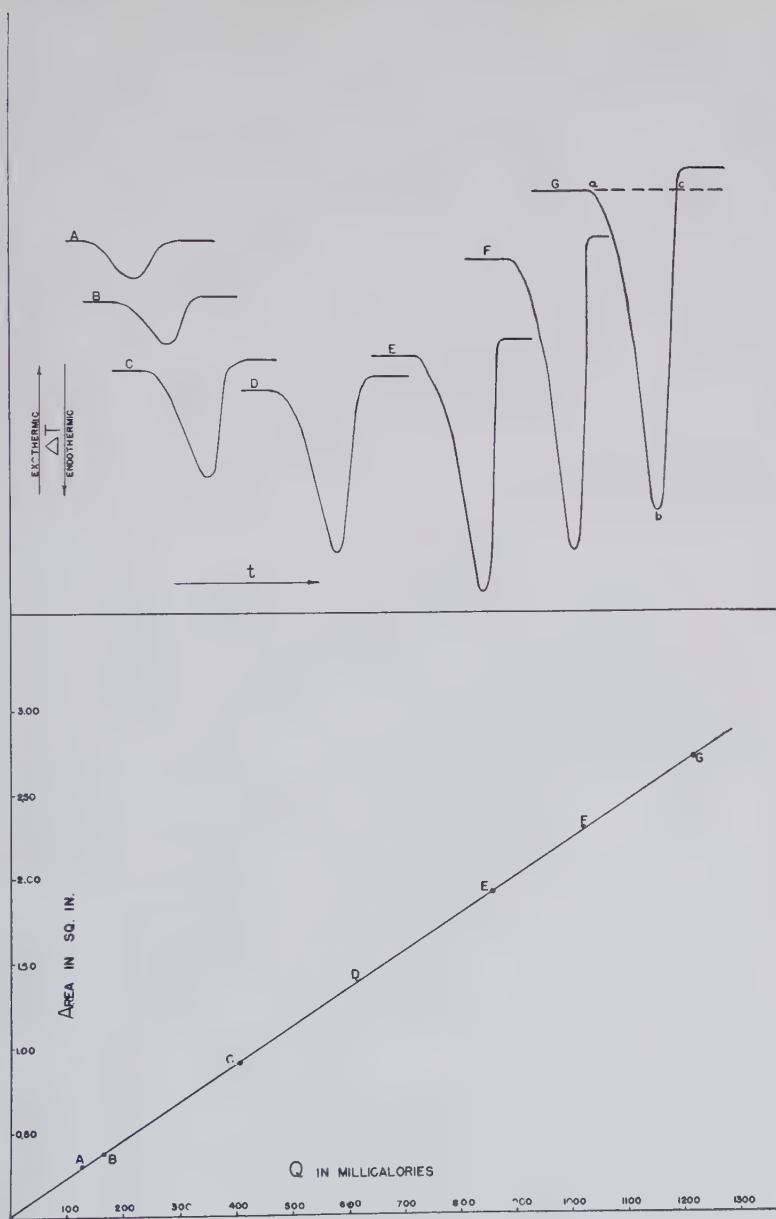


FIG. 3

so that point *a* becomes unidentifiable. The work of Norton<sup>7</sup> and that of Berkelhammer<sup>8</sup> emphasize this fact clearly.

The difficulties of the non-linear base-line are largely obviated by reducing the mass of the furnace housing, employing high heating rates, (30° C. per minute), and testing small samples with large  $\Delta H$ . The reaction point *a*, Fig. 2, is sharply defined as the slope *ab* steepens, and the base-line deviation is reduced to a small magnitude. The method of area measurement adopted overcame this slight deviation as shown in Fig. 3, curve *G*. The base-line is merely extended from point *a*, the reaction origin, to point *c*, where the reaction is completed for all intents and purposes. The area measured is that enclosed by *abc*.

A standard procedure of analysis was established for this investigation and strictly adhered to. The use of uniform thermocouples, precise centering within the furnace wall, careful particle sizing, and uniform packing of samples are the important rules to be followed.

#### DISCUSSION

The results of this experiment justify the belief that a low-mass radiation-type furnace can render important service in investigations of this nature. The sensitivity of the instrument described was found to be 30 to 100 times that of instruments described in the recent literature,<sup>5,7,8,9,10</sup> and it should be mentioned that no amplification was needed to achieve these magnified thermographic curves.

The apparatus described here is an excellent tool in the range 300° C–1100° C. Below 300° C it cannot be used as a quantitative instrument because the mass of the furnace housing is too large to permit sensitive response and control at temperatures this low, especially at high heating rates which have been shown to be desirable in the higher temperature ranges. It is suggested that further diminution of the furnace housing to one having lower inertia may make calorimetric studies over a wider temperature range possible. The possible applications of such a quantitative calorimetric tool are numerous.

<sup>7</sup> Norton, F. H., Critical study of the differential thermal method for the identification of the clay minerals: *J. Am. Cer. Soc.*, **22**, 54–63 (1939).

<sup>8</sup> Berkelhammer, L. H., Differential thermal analysis of quartz: *U. S. Dept. of Int.—Bur. of Mines*, **R. I. 3763** (1944).

<sup>9</sup> Faust, G. T., Thermal analysis studies on carbonates, I. Aragonite and calcite: *Am. Mineral.*, **35**, 207–224 (1950).

<sup>10</sup> Beck, C. W., An amplifier for differential thermal analysis: *Am. Mineral.*, **35**, 508–524 (1950).

## ACKNOWLEDGMENTS

The author is indebted to Professor M. J. Buerger for critically reviewing the manuscript. To Professors W. L. Whitehead and H. W. Fairbairn go the writer's gratitude for helpful advice and full use of the equipment.

A special note of thanks is due Mr. John Solo who gave much technical assistance.

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## NOTES AND NEWS

### DETERMINATION OF THIN SECTION THICKNESS BY THE U-STAGE

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#### INTRODUCTION

In the determination of the thickness of a thin section, frequent use is made of the calibrated fine adjustment screw on the polarizing microscope, focusing on dust particles on the top and bottom of the section or on inclusions in mineral grains. This method leads to results which are not too accurate because the particles usually are not located in the correct places with reference to the top and bottom of the mineral grains.

The color chart of Michel Lévy which has the slide thickness in millimeters as the ordinate and the birefringence as the abscissa is also used. The assumption which is made when this chart is used is that the maximum birefringence is observed in the mineral in question. In the case of quartz, the maximum birefringence is seen only when the optic axis lies in the horizontal plane. If the slide has a "normal" thickness of 0.03 mm. and the optic axis lies in the horizontal plane, then the maximum interference color, which is straw-yellow, is seen. Emphasis must be placed on thickness when this method is used. A slight variation in thickness, even though the optic axis is horizontal, will cause a departure of the interference colors from straw-yellow. Experience has shown that there is a wide variation in thin section thickness when measurements are made at various places in the slide.

#### USE OF THE U-STAGE

An accurate measurement of mineral thickness can be obtained through the use of the universal stage. In this connection, quartz, which is almost always present in a slide, is used as a standard of reference. The function of the U-stage is to place the optic axis of quartz in the horizontal plane by the conventional manipulations. In this position, the maximum retardation can be measured by either a Berek compensator or a graduated quartz wedge and an accurate numerical value of the retardation can be obtained. Since the birefringence ( $n_2 - n_1$ ) of quartz is 0.009, the retardation formula  $R = l(n_2 - n_1)$  can be used to calculate the slide thickness. As an example, if  $R$  is determined to be 270 millimicrons when the optic axis is horizontal and ( $n_2 - n_1$ ) is 0.009 then

$$t = \frac{270}{0.009 \times 10^6} = 0.03 \text{ mm.}$$





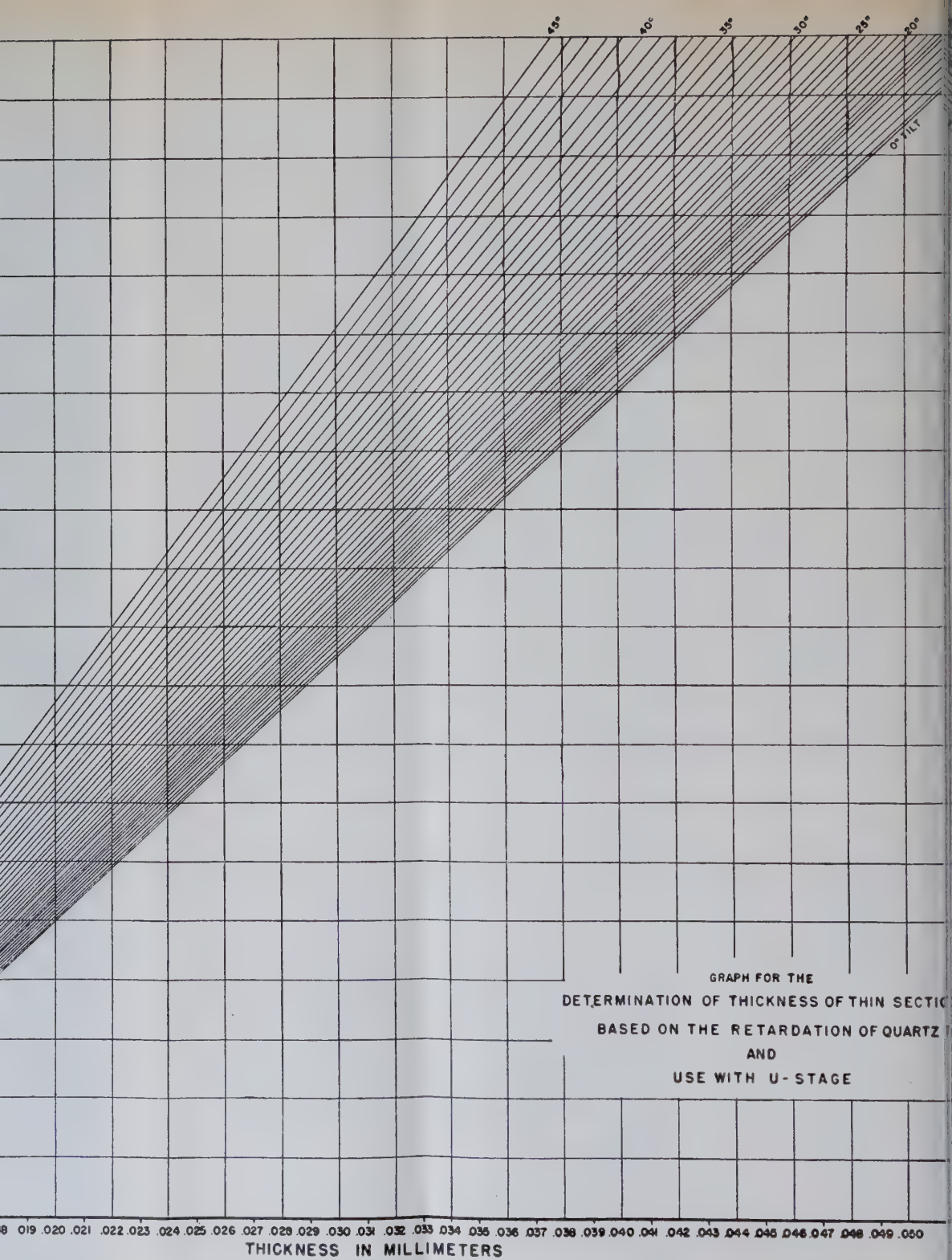


FIG. 1.

Since the formula  $R = t(n_2 - n_1)$  is a straight line curve, a graph can be constructed from which the thickness of quartz for any retardation can be read off.

It is rarely the case that the optic axis of a quartz grain in a slide will lie in a horizontal plane when the axes of the U-stage are at zero. To place the optic axis horizontal involves a tilt on the  $A_2$ -axis of the four-axis stage or the N-S axis of the five-axis stage. Knowing the degree of tilt necessary to make the optic axis horizontal and the retardation, measured when the stage is tilted, it is easy to calculate the retardation and thickness for the section in the zero position. For example, if the stage were tilted 30 degrees and at this position the retardation were measured as 312 millimicrons, then the retardation at the zero position would be  $312 \times \cosine 30^\circ$  or 270 millimicrons. From this, the normal slide thickness of 0.03 mm. can be either calculated or read from the graph.

In order to overcome the need of making calculations after each measurement, a graph (Fig. 1) containing curves for various angular tilts of the U-stage when the quartz optic axis is horizontal has been prepared. In using the graphs the retardation of a quartz grain is measured and the value located along the ordinate of the graph. In order to find the mineral thickness when the slide is at zero tilt, the retardation value is traced horizontally until it intersects the proper curve representing the U-stage tilt. From this intersection a vertical line is projected downward to the horizontal axis where the correct thickness is read off. Using the above retardation as an example, the value 312 is traced across until it intersects the 30 degree curve. This point is traced downward to the H-axis where the value of 0.030 mm. is read off. This means that when a slide of 0.03 mm. thickness is tilted 30 degrees it produces a retardation of 312 millimicrons. If it is desired to know the retardation in the zero position equivalent to the retardation of 312 millimicrons at 30 degrees, then from the intersection of the 312 line with the 30 degree curve, a normal is dropped to the curve representing the zero tilt. From this point a horizontal line will intersect the ordinate at 270 millimicrons. The curves, therefore, will indicate not only the thickness for zero tilt, but also the retardation equivalent to this thickness.

#### CONCLUSIONS

Experience has shown that thin sections are not of uniform thickness. Three recent measurements on a slide of a metamorphic rock gave values of 0.036 mm. in the center of the section, 0.024 mm. halfway to the edge, and 0.018 mm. at the edge. The assumption that a slide is 0.03 mm. is not valid and the figure should not be used if calculations involving thickness are employed.

The method described above can be used for the determination of the alpha index of micas belonging to the biotite group. The gamma index is determined by oil immersion and the retardation is measured when the cleavage has been made vertical. The slide thickness is ascertained by measurements on a nearby quartz grain. Using the retardation formula, the birefringence ( $n_2 - n_1$ ) is calculated from:

$$(n_2 - n_1) = \frac{R}{t \times 10^6}.$$

The value of  $n_2$  is the gamma index; therefore, the alpha index is gamma minus the value of the birefringence determined above. The gamma and alpha values can be used with the four component diagram of Winchell (*Am. Mineral.*, 20, p. 776) to ascertain the theoretical composition of the biotite mica.

#### NOTES ON THE NOMENCLATURE OF TEXTURAL TERMS IN PETROGRAPHY

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The usage of the terms "texture" and "structure" in continental Europe is markedly different from that employed by most North American and British authors. In many instances the European uses the term "texture" where "structure" would be used in this country, and vice versa. Furthermore, differences are noted in the modifying adjectives used in describing the texture of rocks.

Johannsen, in one of the most helpful text-books on the texture and structure of rocks, defines texture as follows: "Texture is used for the smaller features of the rock itself, that is, those features which depend upon the size and shape, and arrangement and distribution, of the component minerals." (Johannsen, A.: *A Descriptive Petrography of the Igneous Rocks*; Vol. I, 2nd. Ed., p. 32.) This textbook includes in a handy Appendix, definitions of 376 textural and structural terms, together with references to the first recorded use of each term.

While comparing the textural and structural terms used by Johannsen and other authors, the writer felt that they could be divided into two main groups. The first group, taken mainly from Latin and Greek words, including terms such as, *intersertal*, *porphyritic*, *fine-grained*, refer to only one property or characteristic of the mineral or rock. The term of the second group, such as *aplitic*, *granitic*, *diabasic*, are derived from rock

names. In contrast to those of the first group, terms of the second group indicate not a singular feature but rather all the textural features of the type rocks from which they are derived. Moreover, when such terms are used mineralogical as well as textural similarities to the type rock are automatically implied.

It would seem advisable to avoid the synonymous use of terms from these two fundamentally different groups. To give a list of synonyms, as Johannsen does, is doubtless very useful if the large number of textural and structural terms is considered; but in some cases it would seem desirable to define more precisely those terms which have similar but not synonymous meanings. With the development of every science the need increases for exact terms sharply defined.

Priority of descriptive terms is recognized in all branches of natural science. However, in petrography the historical priority cannot be adhered to strictly because the microscope was not used until 1858 to reveal with some precision the textural, structural, and mineralogical features of rocks.

Special consideration should be given when similar terms are used with reference to different rock groups. An example is the choice of the terms "automorphic" or "idiomorphic." As the term "idioblastic" is widely used in relation to metamorphic rocks, preference should be given to the term "idiomorphic" in describing igneous rocks, in spite of the historical priority of the term "automorphic."

#### MICROSEPARATION OF MINERALS IN HEAVY LIQUIDS

J. L. RODDA\*

A technique which may save much work and which has been found useful in separating and identifying mineral grains is that of using drops of heavy liquid on a microscope slide. The operations are best performed under a binocular microscope.

A few drops of any suitable liquid, such as methylene iodide, are placed on a microscope slide and a small quantity of the granular material under investigation stirred in with a needle. The heavy particles will quickly settle to the surface of the slide, while the light particles will rise to the center of the drop at the surface.

The float material may then be removed by lightly touching a narrow strip of blotting paper to the top of the drop, leaving the sink material immersed in the drop. Quartz may be easily removed from minor heavy

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minerals by this method. The refractive indices of the heavy minerals may then be compared with that of the liquid by standard procedures or the grains cleaned for further study.

If the float fraction is to be studied, a glass slide is carefully lowered into contact with the top of the drop of liquid, then withdrawn, when a considerable portion of the float material and some of the liquid will be removed and may be studied on the slide.

It will be seen that the liquid serves two purposes: (1) as a specific gravity standard; and (2) as a refractive index standard. An ideal set of liquids should embrace several refractive index standards for each specific gravity value so that indices may be rapidly determined on a freshly separated portion of sample rather than going through the messy operation of cleaning up a fraction and adding new liquid. Pure compounds are preferable to mixtures because of the constancy of their properties, but the number of liquids having specific gravities above 2.0 is limited. Ethylene bromide, bromoform, tetrabromomethane, and methylene iodide will be found particularly useful. Mixtures of ethylene bromide with tetrabromoethane or methylene iodide and of alpha chlornaphthalene with methylene iodide will cover the specific gravity range around quartz and the feldspars, which frequently must be removed in order to study minor constituents. The stability of these mixtures has not been investigated.

The foregoing technique will be found especially useful in conjunction with the Donnay grids<sup>1</sup> where even a determination of properties within wide limits may help in tracing an unknown.

#### DIRECT DETERMINATION OF INTERPLANAR SPACING FROM X-RAY PATTERNS RECORDED ON CHARTS

ROBERT F. SHURTZ, *The Research Laboratory in Ceramics, University of Texas, Austin, Texas.*

The use of the recording x-ray spectrometer which produces powder diffraction patterns on a strip-chart is greatly facilitated by preparing a calibration curve for reading interplanar spacing directly from the recorded pattern. The writer has learned recently that several laboratories in which recording x-ray spectrometers are used do not use these calibration curves so that it seems worthwhile to present a brief description of the procedure which has been applied for the past two years at this laboratory.

<sup>1</sup> A small set of grids for the determination of non-opaque minerals: *Am. Mineral.*, **23**, 91-100 (1938).

Assume, for example, that the x-ray diffraction pattern of a powdered sample is recorded on a strip-chart at an angular scale of  $2\theta = 2^\circ$  per inch, using copper radiation of wave length  $1.5374 \text{ \AA}$ . The calibration curve for patterns made under these experimental conditions is prepared by plotting the value of the interplanar spacing as a function of  $2\theta$  cross-wise on a strip of blank chart. The values of  $2\theta$  are plotted length-wise of the blank chart to a scale of  $2^\circ$  per inch. The values of the interplanar spacings are, of course, most conveniently obtained from tables such as those in "Internationale Tabellen zur Bestimmung von Kristallstrukturen" for Cu  $K_\alpha$  radiation. A smooth curve is carefully drawn connecting the plotted points.

The calibration curve is then placed directly above the chart containing the diffraction pattern on a table which has a straight lower edge as shown in Fig. 1. A T-square with a straight hair-line scribed along the under side of one of the transparent edges is used as shown to read the interplanar spacing for a particular reflection directly from the calibration curve.

The calibration curve should be plotted in sections so as to obtain a reasonable slope. Most charts are marked with ten major divisions across the chart. Each major division is subdivided into ten or twenty minor divisions. The writer has found it convenient to plot interplanar spacings from  $20 \text{ \AA}$  to  $10 \text{ \AA}$  as a section of curve across the full width of the chart. A section of the curve from  $10 \text{ \AA}$  to  $4 \text{ \AA}$  is plotted to the same scale so that in the range from  $4 \text{ \AA}$  up the scale is one major division per Angstrom unit. In the range from  $4 \text{ \AA}$  down the spacing scale is multiplied by ten so that a section of curve across the chart is required for each Angstrom unit and so that each major division on the chart corresponds to  $0.1 \text{ \AA}$ .

Aside from the speed and convenience obtainable in this method there is the additional advantage that it is easy to correct for the slippage that often accumulates between the beginning and the end of a chart. This is accomplished simply by sliding the calibration curve in relation to the diffraction pattern so that calibration marks on the pattern match the proper degree marks on the curve or so that reflections from known substances such as internal standards appear at the correct interplanar spacings. A case of this kind is illustrated in Fig. 1 where slippage of  $0.2^\circ$  has accumulated at the  $(10\bar{1}1)$  reflection of quartz. By adjustment of the calibration curve so as to bring this reflection at  $3.33 \text{ \AA}$  on the curve it is possible to read the spacing for the nearby  $(004)$  reflection of kaolinite correctly at  $3.56 \text{ \AA}$ . Use of the calibration curve has other advantages inasmuch as it enables one to work directly from the *A.S.T.M.* index cards or other lists of interplanar spacings to the diffrac-

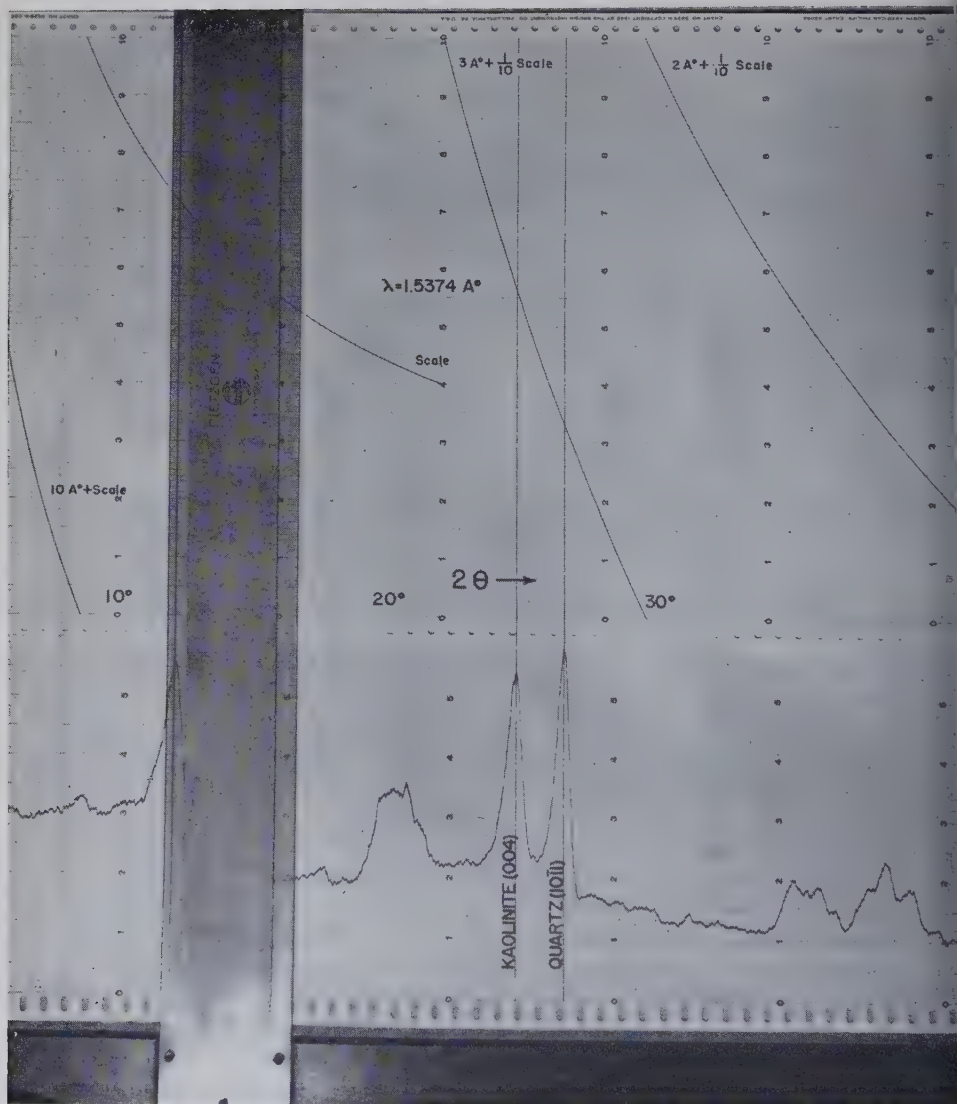


FIG. 1. Arrangement for reading  $d$  directly from strip-chart by use of plotted calibration chart. Scale for  $d$  is vertical on calibration chart. Note how quartz reflection may be used to correct  $0.2^\circ$  slip in pattern.

tion pattern or vice versa. Reflections from known substances may be checked off rapidly, weak and doubtful reflections may be identified rapidly, and the necessity for much tabulation of interplanar spacings and relative intensities disappears because the data can be written directly on the diffraction chart which serves as a most satisfactory record of the experiment.

VIVIANITE CONCRETIONS IN AQUIA FORMATION (MIDDLE EOCENE),  
ANNE ARUNDEL COUNTY, MARYLAND

AUTHUR R. BARWICK\*

Recently, in conjunction with geological field work done for a project sponsored by the Office of Naval Research, the author found some rather large concretionary masses in the Aquia Formation (Middle Eocene) exposed in a roadcut along Tarnan's Branch of the South River, Anne Arundel County, Maryland. More precisely located, the concretions were found on the south bluff of Tarnan's Branch where the Rutland School Road underpasses the new Expressway, now under construction (long.  $76^{\circ} 38' 2''$  W., lat.  $38^{\circ} 57' 58''$  N.).

The concretions vary in size from about 4 to 8 inches in diameter. They are deep blue in color and are often surrounded by a rusty shell of limonitic material. Under the microscope they are found to consist of deep blue needles of vivianite,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ .<sup>1</sup> The largeness of the concretions and their relative abundance seemed to be a matter of sufficient mineralogical interest to deserve mention.

The strata in which the vivianite concretions occur consist of Middle Eocene greensand of Aquia age. In the South River area of Maryland, the Aquia formation consists of a greenish-gray, glauconitic sand, practically free of clay, that is occasionally indurated by limonitic bands that have resulted from the weathering of the contained glauconite partly through exposure during burial but mostly by the subsequent downward percolation of oxygenated meteoric waters. On the surface the soil derived from this formation consists of a light-brown to greenish sandy loam that is known locally as the Collington fine sandy loam. Although the limonitic bands are fairly common and, at times, may contain casts of Eocene molluscan shells such as *Venericardia planicosta*, *Dosiniopsis lenticularis* and *Turritella mortoni*, the above locality is the only one in which the author has found, or has read accounts of others finding, extensive concretions of vivianite. Specimens of these concretions are

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<sup>1</sup> Identification checked by Division of Mineralogy, U. S. National Museum.

being retained for the Museum of Geology, Howard University, Washington, D. C., and the United States National Museum.

#### THE GREENOCKITE LOCALITY AT BISHOPTON, SCOTLAND

H. F. HARWOOD, *Deganwy, North Wales, England.*

In view of the announcement in the January-February issue of *The American Mineralogist*, Vol. 36, 1950, page 165, that crystallized greenockite had been discovered at two new localities in Bolivia, a note of a visit paid last year by the writer and some mineralogist friends to the original Scottish source of this mineral may not be without interest.

The exact locality is a large pasture field near the village of Bishop-ton. Beneath the field runs the railway to Greenock, in a tunnel about 60 feet below the surface; this tunnel was excavated well over a century ago. At about the center of the tunnel is a large "eye" through which a considerable portion of the excavated debris was hoisted to the surface and dumped on the nearby grass field. The tunnel traverses a series of inclined lava beds. It is in one of these that the greenockite occurs. The rock in question is an amygdaloidal labradorite porphyry, containing mammillary prehnite. The greenockite crystals occur invariably in crevices of the prehnite. The mineral appears to be confined solely to the one band of rock, and nothing is known about either the thickness of this, or its exact situation in the tunnel.

An intensive search of the excavated material in the field produced one fair-sized block of this rock, and on carefully breaking this up, four crystals of greenockite were obtained from it. The largest one measured 6×4 mm. but was unfortunately incomplete. The remaining three were smaller, but showed well the hemihedral character of the crystals.

A prolonged search failed to bring to light any more of the prehnite-bearing rock, and as comparatively little of the original spoil heap now remains, most of it was carted away thirty years ago for road material, it seems unlikely that the locality will yield any further specimens of these rare crystals of greenockite.

#### TEN YEARS OF NEW MINERAL NAMES

MICHAEL FLEISCHER\*

The completion of a ten year period of abstracting new mineral names for the *American Mineralogist* caused me to review the results for that period. The following table summarizes my present opinion of the new names that have been abstracted in Volumes 26 through 35

\* Publication authorized by the Director, U. S. Geological Survey.



of the *American Mineralogist*; other reviewers would doubtless have arrived at somewhat different results. It is not proposed to discuss here the philosophy of mineralogical nomenclature.

	Total New Names Proposed	Valid Names	Identical with Known Minerals	Unnecessary Names for Varieties	Insufficient Data
1941	20	8	3	8	1
1942	12	5	1	5	1
1943	14	9	2	1	2
1944	11	7	3	1	0
1945	14	5	2	4	3
1946	11	5	2	2	2
1947	21	9	3	4	5
1948	20	7	2	4	7
1949	22	15	2	1	4
1950	19	7	2	3	7
	164	77	22	33	32

Detailed comments are perhaps unnecessary. New names are being added at the rate of about 20 a year, except for the War years, and less than half of these appear to be valid; very likely some of those above considered valid now will be discredited later. During this same period, 85 mineral names were discredited. It is mildly comforting to note that there were more mineral names discredited than there were valid species established.

There are probably 1200 to 1500 valid mineral species, the exact number depending on the counter's definition of mineral species; yet a complete index of mineralogical names would probably require 10,000 to 12,000 entries. In these circumstances, it behooves every mineralogist to think carefully before he proposes a new mineral name.

#### ABSTRACT

CALCULI AND OTHER STONES FOUND IN MAMMALS, by CHARLES MILTON AND JOSEPH M. AXELROD (U. S. Geological Survey). *Journal of Mammalogy*, May, 1951.

This is a study, using x-ray diffraction patterns, of the substances composing several dozen pathologic stony concretions found in the internal organs (stomach, kidneys, salivary glands, etc.) of deer, horses, mules, and dogs. All available literature is reviewed furnishing additional data on calculi from guanacos, hippopotami, elephants, and many other beasts, birds, and fishes. Of special interest to the mineralogist is the identification of brushite, newberyite, struvite, calcite, whewellite, and weddellite. Four pages of plates with 22 figures show the characteristic aspect and internal structure of the various types of stones; most of which form around a foreign nucleus, such as a wooden sliver, an iron nail, a lead bullet, siliceous hematite, or a whole pecan nut. A brief theoretical discussion of the formation of such calculi, from the standpoint of colloid chemistry, is based largely on the writings of Heinrich Schade, whose work also throws light on lithogenic processes in sedimentary rocks. The former therapeutic use of mammalian calculi ("bezoars," "mad-stones") is discussed and 25 references to the literature of calculi are cited.

## X-RAY IDENTIFICATION AND CRYSTAL STRUCTURES OF CLAY MINERALS.

Edited by G. W. BRINDLEY. London, 1951, *Mineralogical Society* (Clay Minerals Group).

The *Mineralogical Society of Great Britain* announces the publication of a new and original monograph of 345 pages. The preparation of this book results from the efforts and discussions of the Clay Minerals Group which was formed in 1947 for the express purpose of furthering the study of clay minerals.

The book provides an authoritative account of the x-ray identification and crystal structures of clays and allied substances. The fourteen chapters are contributed by a number of different authors who are experts in their respective fields, the co-ordinating editor being Dr. G. W. Brindley. The kaolin, montmorillonite, mica, and chlorite minerals, vermiculite, sepiolite, attapulgite, and oxides of iron and aluminium are all included in the survey. A great deal of information is presented in the form of tables, valuable for reference purposes not only to those concerned with the study and applications of clays, but also to x-ray crystallographers generally.

Copies, price 35s (post free 36s) are obtainable only from the *General Secretary, Mineralogical Society*, British Museum (Natural History), Cromwell Road, London, S.W. 7, or in the U.S.A. (price \$6.00), from *Dr. R. E. Grim, Illinois Geological Survey, Urbana, Illinois, U.S.A.*

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INDUSTRIAL DIAMOND REVIEW—FREE REPRINT SERVICE

A new list of this reprint service which has been organized by Industrial Diamond Review and Industrial Diamond Information Bureau has now been issued. It contains about 187 reprints which are divided into the following subjects: General (Diamond Industry); Physical Properties, etc.; X-ray Crystallography and Radiography; Surface Finish; Diamond Polishing; Shaped Diamond Tools; Truing of Grinding Wheels; Diamond Dust and Diamond Grinding Wheels; Diamond Dies; Cutting and Machining of Glass; Diamond Drilling and Stone Working; Sapphire and Jewel Bearings; Hardness and Wear Testing; Historical Aspects; Use and Care of Diamond Tools.

An Authors' Index and a Subject Index of groups are added. Further, a list of Industrial Diamond Publications as issued by the Industrial Diamond Information Bureau and N.A.G. Press Ltd., is added. The Industrial Diamond Information Bureau, 32-34 Holborn Viaduct, London, E.C.1. has arranged for a mailing list for readers interested in these reprints according to which they can receive reprints of selected groups when they are published.

## BOOK REVIEWS

REPORT OF THE COMMITTEE ON THE MEASUREMENT OF GEOLOGIC TIME, 1949-1950. JOHN P. MARBLE, *Chairman*. Division of Geology and Geography. National Research Council. 118 pp. Paper bound. \$1.00.

The 1950 Report of the Committee on the Measurement of Geologic Time contains the summary report of the Committee by John P. Marble and seven supplementary reports: Progress reports by P. M. Hurley and by L. H. Ahrens; The Pb-U ratios of two Saskatchewan pitchblendes by H. V. Ellsworth; a review of the work in geophysics at the University of Toronto by J. P. Marble (on p. 41 the Iron Hill area is stated as being in Montana, instead of Colorado); recent analyses of radioactive minerals from Brazil by Willer Florêncio and Djalma Guimarães, collated and commented upon by J. P. Marble; the annotated bibliography of articles relating to geologic time compiled by J. P. Marble; and a translation by A. H. Marble of "Age in Years of the Formation of the Elements" by J. M. López de Azcona.

As usual, the bibliography is relatively complete, and the annotations are critical and useful. Many references have been culled from obscure journals that ordinarily do not reach the attention of mineralogists and geologists. The summary report is a worthwhile and newsy rundschau of research activity in all methods and branches of age determination.

E. WM. HEINRICH,  
*University of Michigan*

DIE METALLISCHEN ROHSTOFFE, VOL. 9, BLEI UND ZINK, by G. BERG, F. FRIEDENSBURG, AND H. SOMMERLATTE. Edited by F. Friedensburg. Ferdinand Enke Verlag, Stuttgart, Germany. 1950, 468 pp., 58 figures, 287 tables. DM 73.50.

This is the ninth volume in the encyclopedic series begun by Paul Krusch on "Metallic raw materials, their depositional relationships and their economic significance." Already the work embraces 2031 pages and so far has only treated V, U, Ra, Au, Cu, Mn, Ni, Co, Sb, As, Pb, Zn, Mo, Th and Ce. Volumes on Pt, Hg, Bi, Cr, Ti, Ta, Cb, Sn, and W are announced as planned, so expectations for future production are high indeed. These compendia bid fair to outstrip even the herculean efforts of such gleaners as Hintze and Doelter in mineralogy and Goldschmidt in crystallography, compilers who have long symbolized the ultimate in that peculiar Germanic propensity for the collection and classification of huge accumulations of facts. We can only hope that the future use of these volumes will justify the obviously gargantuan efforts that have been poured into a construction that locally, at least, succumbs to mere non-critical ponderosity. The reader may well be tempted, after wading through a mass of ancient production figures and staggering about in a maze of detailed descriptions of deposits, to scurry on to the back cover without pause. Furthermore, when he notes the frightening price tag attached to this work (approximately \$18), he might in exasperation wonder if the authors were, perhaps, paid by the word. This is a volume that belongs in the library and will probably tend to remain there.

E. WM. HEINRICH,  
*University of Michigan*

METEORITIC DUST, by J. D. BUDDHUE, University of New Mexico Publications in Meteorites No. 2. University of New Mexico Press, Albuquerque, N. Mex. 102 pp. 1950. \$1.50.

According to the author each year the earth receives 35-70 million kilograms of meteoritic dust from space. This material represents, by his theories, particles of the solar dust cloud, meteors and meteorites. It is collected for study from rain water by means of magnets, on sticky slides and glycerine-surfaced plates and from snow and hail (cryoconite). The dust thus obtained consists of spherical particles, cindery fragments and angular grains,

as well as "various kinds of terrestrial contaminants." Apparently the confusion of meteoric dust with meteoritic dust may progress beyond mere nomenclature. The spherical bodies are largely glass, both light and dark colored. A few consist of magnetite. The presence of Ni is doubtful but native Fe seems to form part of the metallic pieces. The particles range from 0.005 to 0.2 mm. in diameter.

After a discussion of the previous studies in this field and an account of collecting methods the author gives detailed physical and chemical descriptions of the captured powder and speculates on its origin, attempting to correlate heavy dust collections with meteoritic showers. Certainly for petrographers and mineralogists interested in meteorites this sabulose little volume provides a worthwhile summary of a relatively neglected phase of extra-terrestrial investigation.

E. WM. HEINRICH,  
*University of Michigan*

AN INDEX OF MINERAL SPECIES AND VARIETIES ARRANGED CHEMICALLY by MAX H. HEY. The British Museum, Cromwell Road, London, S. W. 7, England. 609 pp. £1.10s. 1950.

An unusually useful and usable compilation of mineral names has been completed by M. H. Hey, Principal Scientific Officer in the Department of Mineralogy of the British Museum. The work, which was begun in 1942 as a card catalogue and involved three years of preparation, provides two lists of mineral names. The first index is arranged by chemical groups, for example: Elements and Alloys; Carbides, Nitrides, Silicates, and Phosphides; Sulphides, Selenides, Tellurides, Arsenides, Antimonides, and Bismuthides; Oxy-sulphides; etc. In most of these sections the next subdivision is based on the metal ion contained. Cross references preclude the necessity for more than one main entry in cases of minerals that contain more than one important metallic constituent. Each mineral name entry is given a series of three numbers, e.g., 3.8.6 Alabandite, denotes that Alabandite is classified first under Sulphides-(group) 3, then under Sulphides of Cr, Mo, W, Re, and Mn, (Sub-division) 3.8, and is entry 6. Recognized terminological usage is followed for isomorphous series inasmuch as end-member names are given for some series and intermediate species names for others. Well defined or recognized species names are printed in bold face in order to contrast with the presentation of varieties which are in italics and doubtful and imperfectly described minerals which are in ordinary type. After each listing the formula of the mineral is given or, if the formula is not definitely established, the general composition is discussed briefly. Next follow abbreviated references to the literature to establish the formula and the individuality.

The second list is arranged alphabetically, with species and chemically distinct varieties again appearing in bold face for emphasis. In this list there follow, after each listing, an identity reference and a short statement that consists either of the number under which the mineral is described in list number one, or the synonymic or varietal relations.

It is unfortunate that the compiler has seen fit to reject the Schaller System of adjectival modifiers which is rapidly obtaining general adoption by mineralogists in all parts of the world as a satisfactory scheme for freeing mineralogical nomenclature of its present unwieldy and largely meaningless agglomeration of varietal names. It is only by applying the system of adjectival modifiers that mineralogists can remain consonant with a modern conception of minerals as constituting chemical series.

As a mineralogical dictionary the book fulfills the requirements of completeness, conciseness and convenience. Its essentiality depends upon the extent to which it may become surrogatory for the indexes of more expensive and expanded mineralogical compendia that not only define the species but give other data as well.

E. WM. HEINRICH  
*University of Michigan*

## MINERALOGICAL SOCIETY (LONDON)

A meeting of the Society was held on Thursday, January 11th, 1951, in the apartments of the Geological Society of London, Burlington House, Piccadilly, W. 1 (by kind permission).

### EXHIBITS

- (1) Crystals of analcime and baryte from the trachyte of Traprain Law, East Lothian: by Dr. S. I. Tomkeieff.
- (2) The use of a Laspeyres ocular lens in preference to the Berek compensator: by Dr. A. F. Hallimond.
- (3) Sections and colour photographs of (a) artificial corundum, (b) kyanite-staurolite intergrowth, (c) garnet: by Dr. Francis Jones.

### PAPERS

The following papers were read:

- (1) 'REICHENBACH' AND 'BREZINA' LAMELLAE IN METEORITIC IRONS.

By Dr. L. J. Spencer

Reichenbach lamellae, seen as bands on etched sections, were originally described as enclosed plates of troilite parallel to cube planes in the kamacite-taenite structure, and Brezina lamellae as schreibersite parallel to the rhombic-dodecahedron. These minerals, and also cohenite, have since been observed in both of these and in other orientations. It has sometimes been assumed that bands at right angles indicate orientation on cube planes, but they may also be due to other orientations. On a section parallel to an octahedral plane it is possible only with lamellae parallel to the rhombic dodecahedron.

- (2) SEDIMENTARY INCLUSIONS IN THE HYPERSTHENE-GABBRO, ARDNAMURCHAN, ARGYLL-SHIRE.

By Mr. M. K. Wells

The hypersthene-gabbro contains an abundance of granular basic hornfels inclusions which have all been interpreted in the past as recrystallized basic igneous rocks. Some of these inclusions, particularly banded ones, are now believed to be sedimentary rocks which have suffered considerable metasomatism. The original composition of these xenoliths is largely a matter of speculation. In a few cases the true nature of the original rock can still be assessed: these include altered sandstone, pelitic, semicalcareous and peraluminous sediments. Analyses are given of some of the alteration products, together with full details of the texture and field relationships of each rock type. The significance of this discovery in connection with the problem of genesis of the gabbro is briefly discussed.

- (3) SOME DATA ON SYNTHETIC ALUMINOUS AND OTHER PYROXENES.

By Mr. E. R. Segnit

The limits of solid solution in the clinopyroxene phase in the synthetic system  $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$  have been determined. In the system, diopside-alumina, solid solution extends to 13%  $\text{Al}_2\text{O}_3$ . The field of homogeneity in the ternary system extends on the lime-rich side beyond the join diopside- $\text{CaAl}_2\text{SiO}_6$ .

The influence of these replacements in the diopside structure on the optical properties is indicated.

Some data are also provided on the homogeneity limits in the systems diopside- $\text{Fe}_2\text{O}_3$ , diopside- $\text{TiO}_2$ .



(4) THE PETROLOGY OF THE EVAPORITES OF THE ESKDALE NO. 2 BORING, EAST YORKSHIRE.  
PART III THE UPPER EVAPORITE BED.

By Dr. F. H. Stewart

The bed is 205 feet thick. The upper 83 feet was not cored, and the rocks below this have been divided into three main zones:—a basal anhydritic zone (26 feet); followed upwards by a zone of granular halite (44 feet); and then by a zone of halite with a considerable quantity of clastic material (52 feet).

Petrographic descriptions of the rocks are given. The chief constituents are halite, anhydrite and magnesite. Dolomite is present near the base. Quartz is abundant, and talc is conspicuous in the halite zone. Rinneite occurs through a range of 30 feet in the zone of granular halite. Sylvine and carnallite are present in small quantity. Halite-anhydrite pseudomorphs after gypsum are found in the basal zone. There has been much replacement and recrystallisation since original deposition.

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A meeting of the Society was held on Thursday, March 8th, 1951, in the apartments of the Geological Society of London, Burlington House, Piccadilly, W. 1 (by kind permission).

PAPERS

The following papers were read:

(1) THE SURFACE STRUCTURE OF CRYSTALS.

By Mr. A. F. Seager

A preliminary survey has been made of the detailed surface of a wide range of mineral crystals, including fluorite, topaz, beryl, pyrite, baryte, quartz and apatite. The growth forms or vicinal "pyramids" almost invariably show striations, which are interpreted as due to growth by layer spreading. The growth layers may be polygonal, circular or elliptical and exhibit a symmetry not lower than that of the face on which they are found, if certain irregularities are excepted. Evidence has been obtained of the origin of striations on quartz, topaz and other minerals. A generalized description of crystal growth in terms of layer spreading is suggested.

(2) A NEW OCCURRENCE OF UVAROVITE FROM NORTHERN KARELIA IN FINLAND.

By Mr. Oleg von Knorring

A mineralogical and chemical study has been carried out on uvarovite garnets from Northern Karelia. The chromium garnet, usually considered as a rare member of the garnet group, here occurs as a rock-forming mineral. Physical and optical properties have been determined on three analysed uvarovites with varying contents of chromium and it is shown that a strict linear relationship exists between the chromium content on the one hand and the refractive index, density and unit cell size on the other. Evidence of the metamorphic origin of the uvarovite is adduced.

(3) THE PARAGENESIS OF SYLVINE, CARNALLITE, POLYHALITE AND KIESERITE IN ESKDALE BORINGS NOS. 3, 4 AND 6, NORTH-EAST YORKSHIRE.

By Mr. G. Armstrong, Prof. K. C. Dunham, Mr. C. O. Harvey, Mr. P. A. Sabine and Mr. F. W. Waters

The mineralogy of the Permian evaporite succession as revealed by three Imperial Chemical Industries boreholes is described and an account is included of a lower polyhalite zone and two main and one subsidiary sylvine beds. Kieserite, recorded for the first time from Great Britain, accompanies polyhalite in the Lower Potash Seam, where it ap-

pears to have been the last mineral formed. A partial analysis of polyhalite-kieserite rock and complete analyses of the Middle and Upper Potash Seams and Carnallitic Marl are given.

(4) AN X-RAY STUDY OF WADEITE.

By Mr. J. Shearer, Mr. E. T. Robinson and Mr. J. T. Jefferies. (Communicated by Prof. R. T. Prider.)

Wadeite is ideally  $[\text{K}(\text{Zr}, \text{Ca})\text{Si}_2\text{O}_6]_3$  and has hexagonal cell dimensions  $a=6.88 \text{ \AA}$ ,  $c=10.16 \text{ \AA}$ . Indexed powder data are also given.

(5) ON THE OCCURRENCE OF BAYLDONITE, STOLZITE, HYDROCERUSSITE AND OTHER RARE MINERALS IN THE LAKE DISTRICT.

By Mr. A. W. G. Kingsbury and Mr. J. Hartley

As the result of the finding, in 1947, of the rare lead-copper arsenate, bayldonite, in Brandy Gill, Carrock Fell, by the first author a more comprehensive investigation of the district has been undertaken and a considerable number of rare species, including hydrocerussite, covellite, pseudomalachite, cornwallite, antlerite and mottramite, none of which was previously known to occur in the Lake District, have been found; in addition, new occurrences and a number of definite localities have been found for some of the well-known minerals.

The following paper was taken as read:

(1) SOME PHYSICAL PROPERTIES OF RAW AND CALCINED FLINT.

By Mr. J. H. Weymouth and Dr. W. O. Williamson

Flints from English sea-beaches contain quartz, of which some is very fine-grained. There is no detectable opal or cristobalite. The partial replacement of included rhombohedral carbonate by silica is apparent. Adequate calcination of the flint produces cristobalite, which is first noticed at  $1200^\circ \text{C}$ . The density and refractive index of the flint appear to fall at temperatures much below those necessary to produce cristobalite, i.e., while the material is still quartz. The low densities and refractive indices are ascribed to the development of minute pores. To those pores is ascribed also the brownish turbidity seen by transmitted light. The cristobalite ultimately formed is of anomalously low density and refractive index and shows the brownish turbidity already mentioned. By processes of recrystallisation it becomes clear and its density and refractive index increase to normal values. This is explicable by the disappearance of minute pores. The measured density and refractive index of calcined flint vary sympathetically during the various processes of heat-treatment.

NOTICE

X-RAY IDENTIFICATION AND CRYSTAL STRUCTURES OF CLAY MINERALS

This monograph of 345 pages with 81 text-figures and 66 tables, edited by Dr. G. W. Brindley, was published on March 1st, and will be obtainable only from the General Secretary, Mineralogical Society, British Museum (Natural History), or in the U.S.A. from Dr. R. E. Grim, Illinois Geological Survey, Urbana, Illinois, U.S.A. The price is 35s. (36s. post free), and in the U.S.A. \$6 post free. Each member of the Society will be allowed one copy for personal use at the special price of 25s. (26s. post free), on the strict understanding that it will not be resold for at least 12 months from the date of purchase. Remittance should accompany order, and cheques should be made payable to the Mineralogical Society and not to individuals.

*(Titles and abstracts kindly submitted by G. F. Claringbull, General Secretary).*

## NEW MINERAL NAMES

GREGORIO GAGARIN AND JORGE R. CUOMO, *Algunas proposiciones sobre nomenclatura mineralógica: Comun. Inst. Nacal. Invest. Cienc. Naturales, Museo Argentino Cienc. Naturales "Bernardino Rivadavia," Cienc. Geol., 1, No. 5, 21 pp. (1949).*

The authors have set out to give names to all minerals which now lack them, but which are sufficiently well characterized, *in their opinion*, to merit naming. They also suggest new names for some minerals whose present names are not of the type they consider preferable. Some remarks are perhaps justified.

It seems to me that when a mineralogist describes a mineral, but considers that the description is insufficient to warrant giving the mineral a name, later workers should abide by his decision, except when additional data have been obtained on the mineral or on its analogues. Indiscriminate application of new names results only in burdening the literature.

New names have also been given by Gagarin and Cuomo to many materials previously named by others, simply because the old names did not agree with the authors' concepts of how minerals should be named. This is an indefensible practice.

It seems to me that mineralogists should not feel bound by any names proposed in this paper.

Specific remarks on the new names are given below.

### *A. Changes in Present Names*

#### Colombianite

Name, for the locality, given to gold-amalgam, see Dana's *System*, 7th Ed., Vol. I, p. 105.

#### Aurosirite

Suggested change in name aurosmiridium (Dana's *System*, 7th Ed., Vol. I, p. 111), apparently in order to have the -ite ending. There seems to be no good reason for the change.

#### Iraurite

Name suggested for material from Choroh River, Transcaucasia, analyzed by Chernik: Ir 30.4, Au 62.1, Pt 3.8, Ag 2.1%. An unnecessary name for iridian gold, even if the material were homogeneous.

#### Osirite, Irosite

Names suggested for iridosmine and siserskite, respectively (see Dana's *System*, 7th Ed., Vol. I, p. 111). See remarks above under aurosirite.

#### Rutosirite

Name suggested for the ruthenosmiridium of Aoyama, see Dana's *System*, 7th Ed., Vol. I, pp. 111-113. An unnecessary name.

#### Iridioplatinite, Platinoiridite

Names given to platiniridium (Dana's *System*, 7th Ed., Vol. I, p. 110), the names referring to compositional varieties.

#### Wretbladite

Name given to AsSb=allemontite of Dana's *System*, 7th Ed., Vol. I, p. 130=stibarsen of Wretblad (see *Am. Mineral.*, 26, 456 (1941)). Named for P. E. Wretblad.

**Garibaldite**

Name given to beta-sulfur (see Dana's *System*, 7th Ed., Vol. I, pp. 144-145), found in fumaroles at Vesuvius and Vulcano. Named for G. Garibaldi, 1807-1882, Italian patriot.

**Hondurasite**

Name given to selen-tellurium, described from Honduras in 1890 (see Dana's *System*, 7th Ed., Vol. I, p. 137).

**Pozzuolite**

Name, for the locality, given to the dubious material called Arsenschwefel (see Dana's *System*, 7th Ed., Vol. I, p. 269).

**Genaruttite**

Name given to material from Genarutta, Monteponi district, Sardinia, originally described as cadmiumoxyd by Wittich and Neumann in 1901 (see Dana's *System*, 7th Ed., Vol. I, p. 502) since renamed monteponite by Fairbanks in 1946 (see *Am. Mineral.*, 32, 484 (1947)). Renamed to indicate the locality exactly. Why?

**Pellouxite**

Name given to lime, CaO (see Dana's *System*, 7th Ed., Vol. I, p. 503). Named for A. Pelloux, Italian mineralogist.

**Suomite**

Name given to tantalic ocher, described by Nordenskiöld in 1855, see Dana's *System*, 7th Ed., Vol. I, p. 603. Named for Suomi, the Finnish name for Finland.

**Tinkalite**

A name proposed for the mineral borax. There is no reason for the change, besides which it would cause confusion with tinalconite.

**Clinovariscite**

Name proposed for metavariscite, presumably in an attempt at uniformity of names.

**Clinostrengite**

Name proposed for phosphosiderite, presumably for the same reason.

**Efremovite**

Name proposed for the mineral called calcium ferri-phosphate by Efremov in 1936 (see *Am. Mineral.*, 22, 811 (1937)). Named for N. E. Efremov, Russian mineralogist.

*B. New Names for Previously Unnamed Minerals***Byströmite**

Name given to the monoclinic dimorph of pyrrhotite described by Anders Byström (see *Am. Mineral.*, 30, 724 (1946)).

**Hurlbutite** (= wurtzite 4H)

**Fleischerite** (= wurtzite 6H)

**Buergerite** (= wurtzite 15R)

These names are given to the polymorphs of wurtzite recently described by Frondel and Palache, *Science*, 107, 602 (1948); *Am. Mineral.*, 35, 29-42 (1950). The names are for C.



S. Hurlbut, Jr., Harvard University; Michael Fleischer, U. S. Geological Survey; and M. J. Buerger, Massachusetts Institute of Technology.

DISCUSSION: Frondel and Palache deliberately refrained from naming these. They stated that they were instead following the system for designating polymorphs suggested by Ramsdell, *Am. Mineral.*, **32**, 64 (1947). They further state, "This system is both nomenclature and classification, and is used for the substances at hand although this represents a departure from the traditional practice of applying given names to minerals." It is a pity that this system of nomenclature has been interfered with by this arbitrary naming of these polymorphs.

#### Miltonite

Name proposed for  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , described by Milton (*Am. Mineral.*, **27**, 517 (1942)) as being formed in a thin section when gypsum was overheated. Named for Charles Milton, U. S. Geological Survey.

DISCUSSION: There was no warrant for naming a material for which the namers had no evidence at all that it occurred naturally. It has recently been described as occurring in the deserts of Central Asia; see Popov and Vorobiev, *Mem. soc. russe mineral.*, **76**, 268–270 (1947); *Chem. Abstracts*, **43**, 2897 (1949). Bassanite, described in 1910 as a new form of  $\text{CaSO}_4$ , is the same material (C. Frondel, personal communication) and the name bassanite, used in Dana's *System*, 7th Ed., Vol. II, has priority.

#### Tangenite

Name given to material described by H. Bjorlykke in 1931 and which may be a titanian variety of betafite. See Dana's *System*, 7th Ed., p. 804, analyses 6–8. Named for the locality, Tangen, Norway.

#### Blakeite

Name given to the material described as zirkelite in 1913 by G. S. Blake and G. F. H. Smith, but which differs from zirkelite. See Dana's *System*, 7th Ed., Vol. I, pp. 741–742.

DISCUSSION: The name blakeite was used by Frondel and Pough, *Am. Mineral.*, **29**, 211 (1944) for an iron tellurate, hence cannot be used as here suggested.

#### Chernikite

Name given to an ill-defined mineral containing chiefly  $\text{CaO}$ ,  $\text{WO}_3$ ,  $\text{TiO}_2$ , and  $\text{Ta}_2\text{O}_5$ , described by Chernik in 1927. See Dana's *System*, 7th Ed., Vol. I, p. 741. Named for G. Chernik (or Tchernik), Russian mineralogist.

#### Guimarãesite

Name given to material from Divino de Ubá, Brazil, described by Guimarães in 1926. May be related to ampingabeite. See Dana's *System*, 7th Ed., Vol. I, p. 807. Named for Djalma Guimarães, Brazilian mineralogist.

#### Villiersite

Name proposed for the hydrated nickel silicate described by Partridge in 1943 (see *Am. Mineral.*, **31**, 85 (1946)). Named for J. E. de Villiers, mineralogist, Geological Survey of South Africa, Pretoria.

#### Tschirwinskite

Name proposed for mineral, perhaps  $\text{FePO}_4 \cdot 14\text{H}_2\text{O}$ , incompletely described by P. Tschirwinsky in 1904. Named for P. Tschirwinsky (also spelled Chirvinsky), Russian mineralogist.



**Boldyrevite**

Name given to mineral, related to ralstonite, described by Naboko in 1941 (see *Am. Mineral.*, **28**, 283 (1943)). Named for A. K. Boldyrev, Russian mineralogist.

**Sollyite**

Name given to  $\text{Pb}_3\text{As}_4\text{S}_9$ , described by R. H. Solly from the Binnental, Switzerland. See Dana's *System*, 7th Ed., Vol. I, p. 456.

**Tellite**

Name given to a mineral (sulfosalt?) from the Binnental, Switzerland. See Dana's *System*, 7th Ed., Vol. I, p. 488. Named for William Tell, Swiss patriot.

**Hoppingite**

Name given to scarlet cubes of mercuric iodide, described from Broken Hill, New South Wales, by A. J. Moses, *Am. J. Sci.*, **12**, 98-99 (1906). Named for Roy Hopping, who collected the material.

**Allenite, Kellerite, Comstockite**

Names given as follows: allenite, for E. T. Allen, chemist of the Geophysical Laboratory Washington, D. C., for  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ . Kellerite, for H. F. Keller who described the material from Copaquire, Chile, in 1908, for  $(\text{Mg,Cu})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ . Comstockite, for the locality, for  $(\text{Mg,Cu,Zn})\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , described by Milton and Johnston, *Econ. Geol.*, **33**, 749-771 (1938), from the Comstock Lode, Nevada.

DISCUSSION:  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$  is probably a valid species (see Milton and Johnston for summary of data). The name allenite is inadmissible, since it would result in hopeless confusion among allanite, allenite, and alunite. The name pentahydrate is used for this mineral in Dana's *System*, 7th Ed., Vol. II (C. Frondel, private communication), and is much to be preferred. Kellerite and comstockite are unnecessary names for cuproan and cuproan and zincian varieties.

**Reitingrite**

Name given to the fibrous, radiating form of  $\text{ZrO}_2$ , principal form of  $\text{ZrO}_2$  in the Brazilian deposits, described by Hussak in 1889, and by Hussak and Reiting in 1903, as being distinct from baddeleyite. Named for J. Reiting of Munich.

**Kenngottite**

Name given to amorphous  $\text{As}_2\text{O}_3$ , doubtfully reported by several authors. Named for G. A. Kenngott, German mineralogist of the 19th century. The name had previously been used as a synonym of miargyrite.

MICHAEL FLEISCHER

**Yttrotungstite**

E. H. BEARD, Thorotungstite—a misnomer: *Colonial Geology and Mineral Resources*, **1**, No. 1, 50-51 (1950). Re-analysis of type thorotungstite showed no radioactivity. The supposed thorium is actually rare earths with Y group: Ce group about 3:1. The new name yttrotungstite is suggested.

MICHAEL FLEISCHER

**Oxychildrenite**

A. I. GINZBURG AND N. V. VORONKOVA, Oxychildrenite, a new mineral of the iron-manganese-aluminum phosphate group: *Doklady Akad. Nauk. S.S.S.R.*, **71**, 145-148 (1950), through *Chem. Abstracts*, **44**, 9306 (1950). Prismatic reddish-brown crystals, occurring with triphylite in pegmatite of the Kalbina Mts., E. Kazakhstan, gave the formula  $(\text{Mn, Ca, Mg})_0.2 (\text{Fe, Mn})_2\text{O}_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ . This is equivalent to a partly oxidized childrenite. The x-ray diagrams are very similar, but differ in details. The mineral is orthorhombic, perfect cleavage {001}, less perfect {010}.  $G.=3.205-3.235$ , hardness  $3\frac{1}{2}-4$ . Optically positive; alpha 1.703, beta 1.708, gamma 1.729; 2V 30-33°; pleochroic, pale- to brownish-yellow.

DISCUSSION: This presents a difficult problem in nomenclature, but it would seem reasonable not to use a new name as long as the structure remains essentially unaltered despite the oxidation.

M. F.

**Wurtzite-4H, Wurtzite-6H, Wurtzite-15R**

CLIFFORD FRONDEL AND CHARLES PALACHE: *Am. Mineral.*, **35**, 29-42 (1950).

**Hühnerkobelite**

M. L. LINDBERG: *Am. Mineral.*, **35**, 59-76 (1950).

**Wherryite**

J. J. FAHEY, E. B. DAGGETT AND S. G. GORDON: *Am. Mineral.*, **35**, 93-98 (1950).

**Shandite**

M. A. PEACOCK AND JOHN McANDREW: *Am. Mineral.*, **35**, 425-434 (1950).

**Miserite**

W. T. SCHALLER: *Am. Mineral.*, **35**, 911-921 (1950).

M. F.

**DISCREDITED MINERALS****Tallingite**

F. A. BANNISTER, MAX H. HEY, AND G. F. CLARINGBULL

Connellite, buttgenbachite, and tallingite. X-ray powder photographs show tallingite from Cornwall to be identical with connellite. Chemical tests showed the presence of sulfate.

M. F.

**Thorotungstite**

This name should be dropped, see Yttrotungstite.

M. F.